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Physico-Chemical Studies of the Ni(4-Methylpyridine)$_4$ (SCN)$_2$ A˙ C_6H_6 Clathrate System

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PHYSICO-CHEMICAL STUDIES OF THE $Ni(4\text{-methylpyridine})_4(SCN)_2 \cdot C_6H_6$ CLATHRATE SYSTEM

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A Thesis

Submitted in Partial Fulfillment of the

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ABSTRACT

a brief outline of the history of clathrate compounds is presented. An extensive study of the clathration process was carried out using Ni(4-methylpyridine)$_4$(SCN)$_2$ as the host structure and benzene as the guest molecule. Evidence obtained in this study indicates that the clathration process for this guest and host pair is other than a first order, reversible reaction. A modified mechanism for clathration is proposed. In addition, it is shown that the data will fit a simple adsorption isotherm.

A crystal lattice change in going from complex to clathrate is confirmed by x-ray powder diffraction patterns. The heat of solution measurements indicate that the nature of the interaction between the guest and the host in the clathrate could be charge-transfer but the evidence is not conclusive. Finally, magnetic susceptibility measurements confirm that the environment about the nickel atom does not change as a result of clathration.

TO MY DEAREST PARENTS

ACKNOWLEDGEMENTS

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HISTORICAL BACKGROUND

HISTORICAL BACKGROUND

Compounds of the type which are now called clathrates have been known for over one hundred years. The word "clathrate" was first introduced into the literature by Powell following his X-ray studies on a series of molecular compounds(26). Powell defined clathrates(from the Latin "clathratus" meaning enclosed or protected by the crossbars of a grating) as "compounds in which two or more components are associated without ordinary chemical union but through complete enclosure of one set of molecules in a suitable framework structure formed by another". Following the work of Powell other investigators began intensive studies on this new type of compound. The early work was divided among the following three areas:

1. Gas hydrates
2. Quinol complexes
3. $Ni(CN)_2NH_3 \cdot M$(M=organic adduct)

1. Gas hydrates

The first gas hydrate of chlorine and water was reported by Davy in 1810(5). Faraday proposed the formula $Cl_2 \cdot 10H_2O$(13). Additional work in this field has shown that this type of hydrate can be formed with a large number of gases or volatile liquids such as Cl_2, Br_2, H_2S, SO_2, Kr, Xe, Ar, CH_4, CH_3Cl and $CHCl_3$.

According to the X-ray crystal analyses of Pauling and

Marsh(25), all gas hydrates crystalize in the cubic system and guest molecules are situated in cavities formed by a framework of water molecules(the host) linked together by hydrogen bonds.

2. Quinol complexes

The first report of these complexes was made by Wohler and Clemm(39, 4) as long as 100 years ago. More recent work in this area has been done by Powell and coworkers(22, 23) (26-33) including the complete structure analysis by X-ray diffraction. Powell proposed that hydroquinone molecules were linked together by means of hydrogen bonds to form a pair of three dimensional networks. The networks, however, do not fill all the available space. The cavities which result are bounded by two circles of six hydrogen bonded hydroxyl groups and by the benzene rings of six quinol molecules. The guest molecules are trapped in these cavities.

Further work by Evans and Richards(9-12) and others(6-8) in this area has been mainly concerned with thermodynamic and other related properties.

3. $Ni(CN)_2NH_3$ complex

The clathrate formed between this inorganic complex and benzene was first reported in 1897. Afterwords this clathrate was the object of thorough investigations by various workers(1). In 1952, Powell and Rayner reported the crystal structure of the $Ni(CN)_2NH_3$·benzene clathrate by X-ray analysis. (34) The compound $Ni(CN)_2NH_3$ has a cage like structure in which guests

such as benzene, thiophene, furan, pyrrole, aniline or phenol are enclosed. The crystal structure of $Ni(CN)_2NH_3$·benzene was worked out in greater detail by Bhatnager(2). The structure is tetragonal and the unit cell contains atoms corresponding to twice the formula. When benzene is enclosed in the complex, each benzene molecule is comparatively remote from any Ni atom. It is contained in a cavity where it makes contacts at vander waal's distances with other benzene molecules and with atoms of the cyanide and ammonia groups.

Following these early investigations a large number of Werner complexes have been shown to function as hosts. Schaeffer and William(35, 38) listed as many as 40 complexes of first row transistion metals that were reported to act as hosts. Hart, Minton and Smith(15, 16, 20, 21) have published thermodynamic constants, kinetic rate data, infrared spectra and phase diagrams for several clathrates formed by Ni(4-methylpyridine)$_4(SCN)_2$ as host. The work by Belitskus, et. al. (1), involved x-ray analysis of the single crystals of clathrates formed by cobalt and nickel tetra-4-methylpyridine dithiocynates. The recent work by Lok(18) showed that there is a definite size relationship between guest and host.

From a study of published articles it soon became apparent that not all of the substances under study were "clathrates" by the original definition of Powell. The need for a classification scheme was evident and the following was proposed:

1. Complex molecules

   A. Coordination Compounds

   B. Inorganic Polymers

   C. Molecular Compounds

      1. Inclusion compounds

         a. Urea and Thiourea Adducts

         b. Zeolite Complexes

         c. Graphite and Silica Complexes

         d. Dextrin-Iodine Type Complexes

         e. Clathrates

Inclusion compounds possess characteristic cavities and are distinguished by the nature of the cavity.

At the present time there is some indication that this classification scheme is not inclusive and will need modification (40).

INTRODUCTION

INTRODUCTION

Schaeffer and co-workers(35) published a paper, entitled "Separation of Xylenes, Cymenes, Methyl-naphthalenes and Other Isomers by Clathration with Inorganic Complexes", in the year 1957. This marked the beginning of a new series of inorganic complexes which can be used as hosts in the process of clathration. Since that time a large number of inorganic complexes have been prepared and their physical and chemical properties studied, including unit cell, dimensions for the crystals. According to the paper by Schaeffer(35) as many as 40 complexes of the first row transition metals are capable of forming clathrates. The clathrates were prepared by two different methods, the suspension process and the solution process. Both processes were utilized in the present work. The work by Schaeffer was only analytical in nature, as his paper deals exclusively with the enrichment of petroleum fractions. Further work by Lok(18) revealed that not all the complexes, listed in Schaeffer's paper form clathrates, at least not by the suspension process. Up to now the only complex which has been studied in greater detail is $Ni(4\text{-methylpyridine})_4(SCN)_2$. Hart in his Ph.D. thesis(15), presented the infrared spectra, phase diagrams and calorimetric data for clathrates of $Ni(4\text{-methylpyridine})_4(SCN)_2$. Minton in her Ph.D. thesis(20), presented the results of further kinetic, phase, and calorimetric studies. Casellato and Casu in their paper(3), made additional studies of the infrared

spectra of clathrates of Ni(4-methylpyridine)$_4$(SCN)$_2$. X-ray studies by Hart(15) also indicated a difference between the crystal structure of the complex and that of the clathrate. The suspected octahedral configuration of the complex was confirmed by magnetic susceptibility measurements and visible absorption spectra. Later, X-ray single crystal studies by Belitskus and others(1) also indicated an octahedral configuration.

Minton in her thesis(20) presents evidence to show that clathration is apparently a first-order, reversible process for p-xylene and ethylbenzene as guests. Lok however, in his thesis(18), presents evidence indicating that clathration is not a first-order, reversible reaction. Therefore it became apparent that further investigations into the rate processes of clathration were needed. The various factors thought to affect the rate of clathration are (i) size of the host crystals, (ii) concentration of the host, (iii) concentration of the guest compound, (iv) temperature, and (v) rate of stirring.

In this thesis, experiments were designed that would test all of the above factors. This was accomplished by kinetic rate studies of clathration using Ni(4-methylpyridine)$_4$-(SCN)$_2$ as host and benzene as guest.

Heats of solution for clathrates of Ni(4-methylpyridine)$_4$-(SCN)$_2$ in dichloromethane were also obtained using a solution

calorimeter. The magnetic susceptibility of Ni(4-methylpyridine)$_4$-(SCN)$_2$ and several of its clathrates was also measured.

INSTRUMENTATION

INSTRUMENTATION

Temperature

A constant temperature bath capable of regulation to ±0.2°C was used for all of the kinetic rate studies.

X-ray Measurements

The X-ray powder diffraction patterns were obtained on a Siemens Kristalloflex 4, X-ray Diffractometer, using copper K-alpha radiation and a nickel filter. A Siemens two radian camera was used and line measurements were made with a coincidence scale having an accuracy of ±0.01 mm.

Spectral Measurements

Ultraviolet spectra were obtained on a Beckman DB-G Grating Spectrophotometer, using Beckman silica cells. A Sargent Model SRL Recorder was used to record the spectra.

Analytical Measurements

An Ainsworth Type 21N single pan automatic balance was used for all weighings.

Heat of Solution Measurements

Heats of solution were obtained from a Guild Solution Calorimeter utilizing a thermistor for temperature measurements. A Leeds and Northrup Model 8687 Potentiometer and a Sargent Model SRL Recorder completed the assembly.

Magnetic Susceptibility Measurements

Magnetic susceptibilities were obtained from an Ainsworth Type DLB chainamatic balance and Atomic Laboratories Electromagnet.

EXPERIMENTAL

EXPERIMENTAL

Preparation of $Ni(4\text{-mepy})_4(SCN)_2$

To 0.228 moles of $NiCl_2 \cdot 6H_2O$ dissolved in three liters of water was added 0.456 moles of KSCN. After complete solution of the metal chloride and thiocynate, 0.910 moles of 4-methylpyridine was added slowly with constant stirring. The mixture was then stirred for an additional hour before filtering. The precipitate was air dried for 4-6 hours and then transfered to a dessicator and stored over solid KOH. Removal of all moisture took approximately 5-7 days. The chemicals used in the preparation of the complex were Reagent Grade and the purity of the complex was checked using standard analytical methods. The large amount of water used in the preparation was necessary to prevent the co-precipitation of thiocyanate.

Purification of Solvent

It was necessary to purify the Reagent Grade heptane before it was used as a suspension medium in the kinetic rate studies. The purified heptane was found equal in quality to the commercially available Spectroquality Grade heptane. The precedure used in the purification was as follows. First, the heptane was extracted using concentrated sulphuric acid. This was accomplished in a large separatory funnel with occasional shaking over a period of twenty four hours. The heptane layer was then neutralized with 10% sodium carbonate followed by a salting out process using saturated sodium

chloride solution. The heptane was then dried by passing through a column of anhydrous clacium chloride and finally fractionally distilled. The purity of the heptane was estimated using ultraviolet spectra.

Preparation of Clathrates for Heat of Solution Measurements

The clathrates for this study were prepared by crystallization from a hot solution of methanol(100 ml) containing the complex (0.004 moles) 0.1 mole of aromatic compound to be clathrated and 0.1 mole of 4-methylpyridine. The crystals were air dried to remove any excess of solvent.

Kinetic Rate Studies

The kinetic rate studies were carried out in a thermostat capable of regulation to ±0.2°C.

A 500 ml reaction flask containing 300 ml of purified heptane was placed in the thermostat and allowed to come to equilibrium. Ten milliliters of benzene was then introduced and the solution was stirred by means of a magnetic stirrer placed beneath the bath. When thermal equilibrium was obtained 1 ml of sample solution was withdrawn by means of a filter stick. 0.1 ml of the withdrawn sample was pipetted into a 25 ml volumetric flask by means of a micro-pipet and diluted with purified heptane.

After the initial sample had been withdrawn the solid $Ni(4\text{-mepy})_4(SCN)_2$ was introduced into the reaction vessel. An amount slightly less than 1:1 mole ratio of guest to host was used. The initial time for the kinetic run was

taken as the time the complex was added to the solution.

Using pre-selected time intervals, 1 ml samples of solution were withdrawn from the reaction flask by means of filter sticks and exactly 0.1 ml of each of these samples was then transferred to a 25 ml volumetric flask and diluted with purified heptane.

Each of the kinetic runs was allowed to proceed for not less than 48 hours. The decrease in benzene concentration as a function of time was determined spectrophotometrically using a Beckman DB-G Spectrophotometer operating in the ultraviolet region at pre-selected wavelengths. The region for benzene was 270 mμ to 240 mμ with a maximum absorbance at 255 mμ. Following each of the kinetic runs the contents of the flask were filtered and the solid material air dried. The solid material was then analyzed for nickel content and an x-ray powder diffraction pattern taken.

X-ray Diffraction Patterns

Samples of each of the complexes and the solid remaining after the kinetic runs were used for powder diffraction x-ray patterns. The samples were prepared by mixing the powdered sample with collodion and extruding the partially dried samples from a 0.5 mm diameter capillary tube. Patterns were obtained with a standard two radian camera using filtered copper K-α radiation and exposure times of one hour.

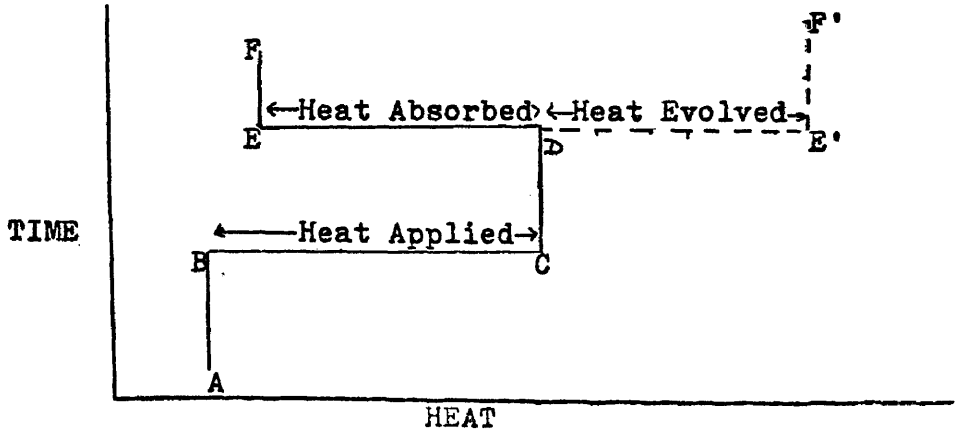
Quantitative Analyses

The percent of nickel in the complex and in the clathrates

was determined by standard procedures(44, 43). The procedure followed in the volumetric analysis was to titrate the nickel solution with EDTA solution using murexide as indicator. Dilute hydrochloric acid was used to breakdown the complexes and clathrates. The percent of nickel in the complex was used as an indication of the purity of the complex. The results are shown in Table I, page 22 .

Calorimetric Studies

Two hundred milliliters of a one percent solution of 4-methylpyridine in dichloromethane was placed in the Dewar flask and the solution was stirred by means of a specially designed glass stirrer. Solid samples were introduced by depressing the plunger of the sample holder, which was especially made for the purpose from a polyethylene syringe, and which was mounted in the cover of the Dewar flask. Liquid samples were introduced by means of a 5 cc Hamilton hypodermic syringe. All measurements were carried out at room temperature. The following Figure is a representation of the type of data obtained in the calorimetric studies.



After a stable base line had been established, that is from A to B, a known amount of heat was applied at point B to the solution in the Dewar flask. This was done by means of an internal heater. When once again a stable base line is obtained(CD), the sample was introduced at point D; heat was evolved or absorbed from the solution depending on the nature of the sample from D to E' or D to E respectively. A stable base line from E to F or E' to F' marks the end of measurements. Calculation of the heat of solution from the recorded data is shown in Appendix II.

Magnetic Susceptibility Measurements

Magnetic susceptibilities of complex and clathrates were obtained from an Ainsworth Model DBL chainomatic, Gouy-type magnetic balance, calibrated with solid $HgCo(SCN)_4$. The electromagnet used was made by Atomic Laboratories Inc., and had a field strength between the poles of 4.7 kilo-gauss for this measurement. All measurements were made at room temperature. The sample holder was approximately 9 cm in length and had a volume of 4.22 ml.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Kinetic Studies

The first kinetic studies on Werner complex clathrates were reported by Gawalek and Könnecke(14). As a result of their studies they reported that the time required for clathration was less than 15 minutes in mostcases and that an important factor which influences the rate is the solubility of the complex. Further rate studies were done by Minton and Smith who reported an apparent initial increase in guest concentration and attributed this to either adsorption or absorption of heptane by the complex. This initial rise was ignored by them for plotting purposes. Lok(18) attributed this initial rise in concentration to an excess of 4-methyl pyridine and suggested that this can be eliminated by extracting the solution with 6N HCl. Minton and Smith further reported that the clathration process appeared to follow first order, reversible kinetics. According to the work of Hart and Smith(16) a lattice change occurs during the clathration process. Using the symbol α for the complex lattice and β for the lattice of the clathrate, the following equation can be used to represent the clathration process:

$$\text{Complex}(\alpha) \longrightarrow [\text{Complex}(\beta)] \longrightarrow \text{Clathrate}$$

Minton(20) reported that the clathration reaction was complete in 4 to 6 hours depending on the particular guest molecule. The process was described as follows: "the clathration reaction would not begin until the guest molecules could

displace solvent molecules, come in contact with the complex, dissolve it to some extent and bring about the lattice change by precipitation. Then, when the lattice change was at least partially accomplished the guest molecules could move into the host". However, work by Jacobs and Lok(17) indicates that the clathration reaction is not a first order, reversible reaction when using p-xylene as the guest. Consequentely it was decided that further, more extensive and detailed studies should be made in an attempt to clarify the rate process involved in clathration. Some of the factors which were thought to influence the rate of clathration are:

(i). Temperature

(ii). Concentration of the guest component

(iii). Rate of stirring of the mixture

(iv). Particle size of the host crystals

(v). Concentration of the host molecules

Each of the above was investigated using benzene as the guest molecule and $Ni(4\text{-mepy})_4(SCN)_2$ as the host crystal.

Temperature

The effect of temperature on clathration was studied from 5°C to 45°C in 10°C intervals. The change in guest concentration(measured as a decrease in absorbance) with time during the clathration process is shown in Table II. The results of the volumetric analyses are presented in Table I and the x-ray analyses in Table III. Figures 1 and 2 represent the results of the kinetic rate studies.

TABLE I

VOLUMETRIC ANALYSIS FOR Ni IN THE COMPLEX $Ni(4\text{-mepy})_4(SCN)_2$ AND BENZENE CLATHRATES

		PERCENT NICKEL				
TRIAL	COMPLEX	CLATHRATE I*	II*	III*	IV*	V*
1	10.72	10.48	10.29	10.02	9.98	10.24
2	10.68	10.48	10.36	10.11	9.98	10.34
3	10.70	-	-	-	-	-
AVERAGE	10.70	10.48	10.33	10.06	9.98	10.29
Theoretical	10.73					
MOLE RATIO+(GUEST/HOST)**		0.186	0.298	0.500	.559	0.328

+ The values are reliable to an extent of ±0.06 units.

* Clathrate I, II, III, IV, and V refers to the clathrate formed at 5°C, 14.8°C, 24°C, 35°C, and 45°C respectively.

** For calculations of GUEST/HOST mole ratio see Appendix I.

TABLE II

CHANGE OF GUEST CONCENTRATION* WITH TIME
DURING THE CLATHRATION REACTION BETWEEN
$Ni(4\text{-mepy})_4(SCN)_2$ AND BENZENE

TIME(HOUR)	ABSORBANCE OF BENZENE AT 255 mu				
	SAMPLE I(5°C)	SAMPLE II(14.8°C)	SAMPLE III(24°C)	SAMPLE IV(35°C)	SAMPLE V(45°C)
0	0.296	0.296	0.297	0.297	0.301
¼	0.282	0.292	0.286	0.301	0.308
½	0.293	0.282	0.291	0.301	0.319
1	0.284	0.277	0.288	0.297	0.328
2	0.298	0.274	0.291	0.310	0.328
3	0.281	0.262	0.292	-	-
4	0.261	0.242	0.272	0.297	0.276
6	0.235	0.221	0.246	0.240	0.256
8	0.223	0.213	0.231	0.223	0.253
10	0.213	0.211	0.217	0.223	0.252
12	0.199	0.208	0.212	0.220	0.252
24	0.197	0.204	0.210	0.220	0.252
48	0.195	0.202	0.210	0.220	0.252

*For calibration curve see Appendix 3.

TABLE III

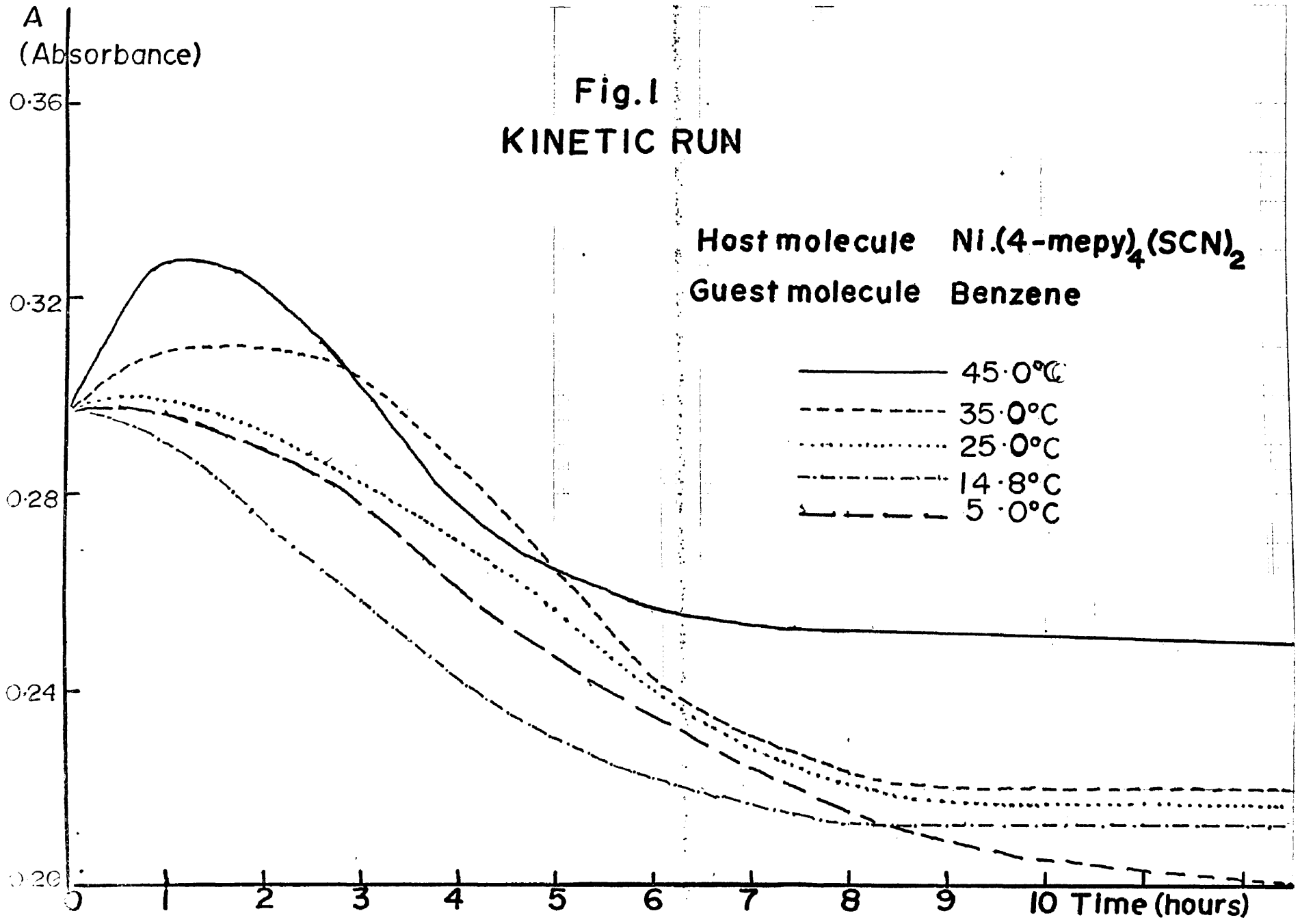
INTERPLANAR SPACINGS(Å) FOR THE MORE PROMINENT REFLECTIONS FROM THE $Ni(4\text{-mepy})_4(SCN)_2$ COMPLEX AND THE BENZENE CLATHRATE

TEMPERATURE STUDY

COMPLEX		CLATHRATE				
obsd	Lit**	I*	II*	III*	IV*	V*
	8.64s	13.13s	12.63s	13.12s	12.63s	12.63s
8.31s	8.37vs	8.04s	8.06s	8.04s	8.04s	8.04s
7.61w	7.56m	6.81w	6.77w	6.80w	6.86w	6.86w
	7.34w	5.80m	6.23m	5.81m	6.09m	6.09m
	5.17w					
	5.03s	5.06m	5.02m	5.10m	5.06m	5.06m
4.98w	4.98m					
	4.85m	4.60w	4.74w	4.73w	4.79w	4.79w
	4.50s	4.50s	4.51s	4.44s	4.44s	4.49s
4.30s	4.36s					
	4.27s					
4.07w	4.08m					
	4.05m					
	3.90m					
3.86w	3.85m	3.78m	3.88m	3.83m	3.86m	3.90m
	3.65w					
3.55w	3.55w	3.55m	3.57m	3.53m	3.55m	3.53m
	3.27w					
	3.16w					

*Clathrate I, II, III, IV, and V refers to the clathrate formed at 5°C, 14.8°C, 24°C, 35°C, and 45°C respectively.

**M. I. Hart and N. O. Smith, J. Am. Chem. Soc., 84, 1816(1962).


A
(Absorbance)
0·36
0·32
0·28
0·24
0·20
0
1
2
3
4
5
6
7
8
9
10 Time (hours)
Fig. I
KINETIC RUN
Host molecule Ni.(4-mepy)4(SCN)2
Guest molecule Benzene
45·0°C
35·0°C
25·0°C
14·8°C
5·0°C

In Figure I, it can be observed that in general there is an initial rise in the concentration of guest molecules. This initial rise seems to increase with temperature except for the kinetic run at 15°C. It can also be cited that the decrease in guest concentration is not observed until about 2 hours into the run. Therefore this period can be assumed to be the time required for initiation of clathration; that is the time required for guest molecules to displace the solvent molecules and to come in contact with the complex. This could also be thought of as an induction period. An increase in initial concentration of guest molecules with temperature can be attributed to the increased adsorption or absorption of solvent molecules. Figure 2 represents a plot of $+\log(A_t-A_e)$ vs time at various temperatures. From the curves obtained it would seem that the reaction is not first-order. In each case however, there is a small region in which the reaction appears to follow a first order rate law. Slopes were measured in this region and rate constants were claculated. The values obtained did not show any regular trend. The rate constant decreased as the temperature was increased up until 25°C. This was expected as the clathration process is exothermic. This is again clear from Table II which shows that the extent of clathration decreases from 5°C to 45°C during the same period. Temperature seems to play a decisive role above 25°C as the k value first increases and then decreases again. An Arrehenius plot was made for the k values at 25°C, 15°C and 5°C. The failure to obtain a

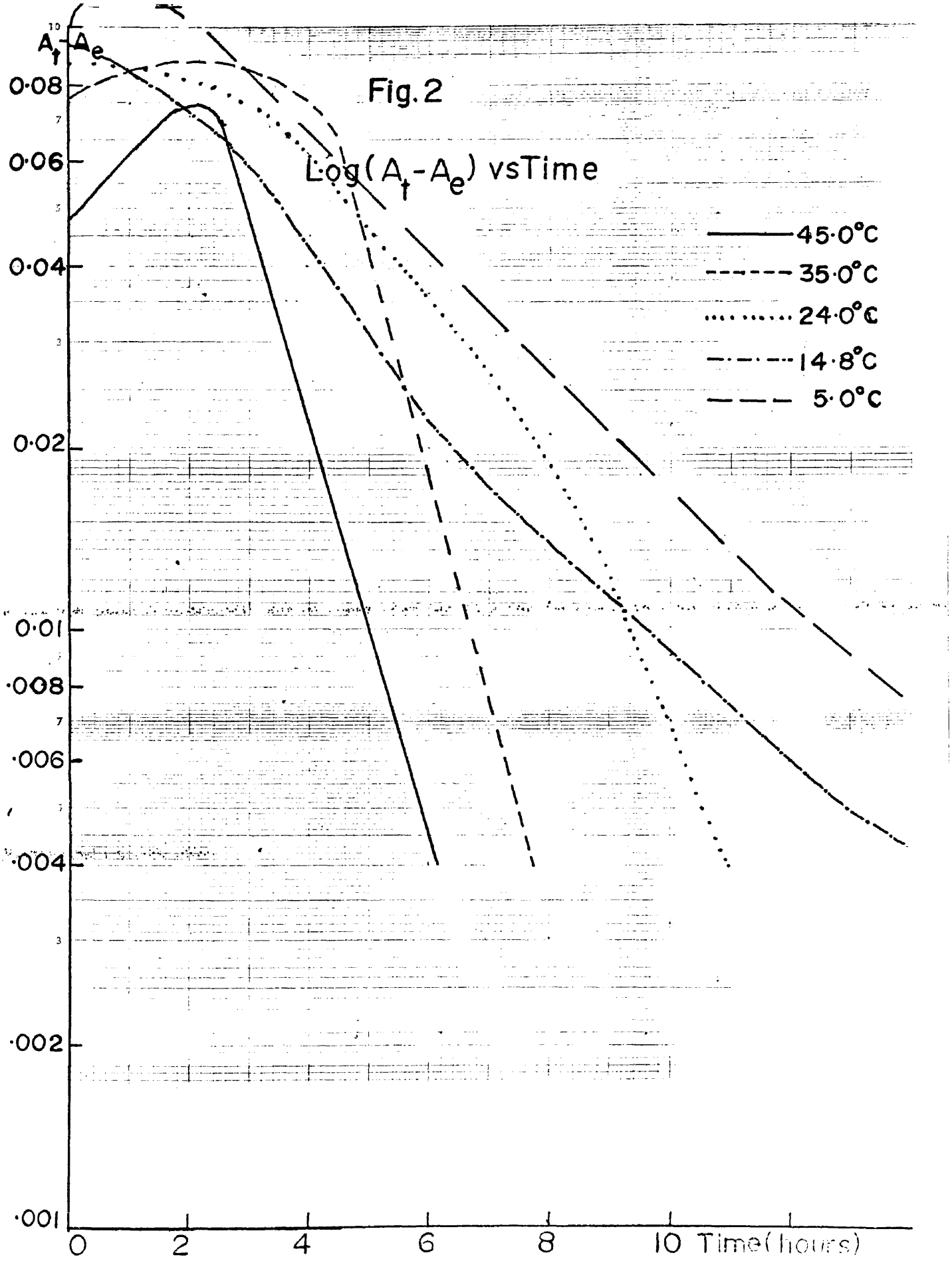


Fig. 2
Log ($A_t - A_e$) vs Time
45·0°C
35·0°C
24·0°C
14·8°C
5·0°C
$A_t - A_e$
0·08
0·06
0·04
0·02
0·01
·008
·006
·004
·002
·001
0
2
4
6
8
10 Time (hours)

straight line again indicates that the reaction is apparently not of first order. These factors would however, support the possibility that the reaction may be simple adsorption.

Concentration of the guest

The effect of the guest concentration on the clathration process was studied by simply varying the guest concentration from 1.66 to 6.66% by volume. The results of volumetric analyses for Ni, and the x-ray analyses are presented in Tables IV and V respectively. The change of guest concentration(measured as decrease in absorbance) is presented in Table VI and a plot of $+\log(A_t-A_e)$ vs time in Figure 3. From the ploted curves it is again clear that the reaction is not first order except perhaps at very high concentration of the guest. At high concentrations it is apparently pseudo first-order and the reaction is complete in about two hours. The reason for this behaviour is apparently due simply to the large excess of guest molecules competing with solvent molecules to dissolve the complex. This is also in agreement with the results of Gawalek(14) who points out that the solubility of the complex in the hydrocarbon greatly effects the rate of formation of clathrates.

Rate of Stirring

The effect of stirring rate on the clathration process was studied in a wide range of stirring speeds. The results of the volumetric analyses, the x-ray analyses and a plot of

TABLE IV

VOLUMETRIC ANALYSES FOR Ni
IN THE BENZENE CLATHRATE

		PERCENT Ni		
TRIAL		CLATHRATE I*	II*	III*
1		10.06	10.02	9.73
2		10.14	10.11	9.73
AVERAGE		10.10	10.06	9.73
THEORETICAL	10.73			
MOLE RATIO(GUEST/HOST)		0.470	0.500	0.746

*Clathrate I, II, and III refers to the clathrate formed at benzene concentration of 1.66, 3.66, and 6.66% to start with.

TABLE V

INTERPLANAR SPACINGS(Å) FOR THE MORE PROMINENT REFLECTIONS FROM THE $Ni(4\text{-mepy})_2(SCN)_2$ COMPLEX AND THE BENZENE CLATHRATE (CONCENTRATION STUDY)

COMPLEX	CLATHRATE		
obsd	I*	II*	III*
	13.06s	13.12s	12.57s
8.31	8.04s	8/04s	8.04s
7.61	6.82w	6.80w	6.81w
	5.99m	5.81m	5.82m
	5.06m	5.10m	5.13m
	4.73w	4.73w	4.70w
4.98	4.44s	4.44s	4.40s
4.30			
4.07			
3.86	3.94m	3.83m	3.91m
3.55	3.52m	3.53m	3.56m

* Clathrate I, II, and III refers to clathrates formes at Benzene Concentration of 1.66, 3.66, and 6.66% respectively to start with.

TABLE VI

CHANGE OF GUEST CONCENTRATION* WITH TIME DURING THE CLATHRATION REACTION BETWEEN $Ni(4\text{-mepy})_4(SCN)_2$ AND BENZENE AT 25°C

TIME(HOUR)	ABSORBANCE OF BENZENE AT 255 mu		
	SAMPLE I*	SAMPLE II*	SAMPLE III*
0	0.152	0.297	0.588
¼	0.154	0.286	0.561
½	-	0.291	0.517
1	0.158	0.288	0.474
2	0.159	0.291	0.458
3	0.158	0.292	0.469
4	0.162	0.272	0.469
6	0.155	0.246	0.467
8	0.152	0.231	0.469
10	0.144	0.217	0.477
12	0.119	0.213	0.469
24	0.087	0.210	0.488
48	0.087	0.210	0.488

Sample I, II, and III refers to the clathrate formed with benzene concentration of 1.66, 3.66, and 6.66% respectively

*For calibration curve see Appendix III

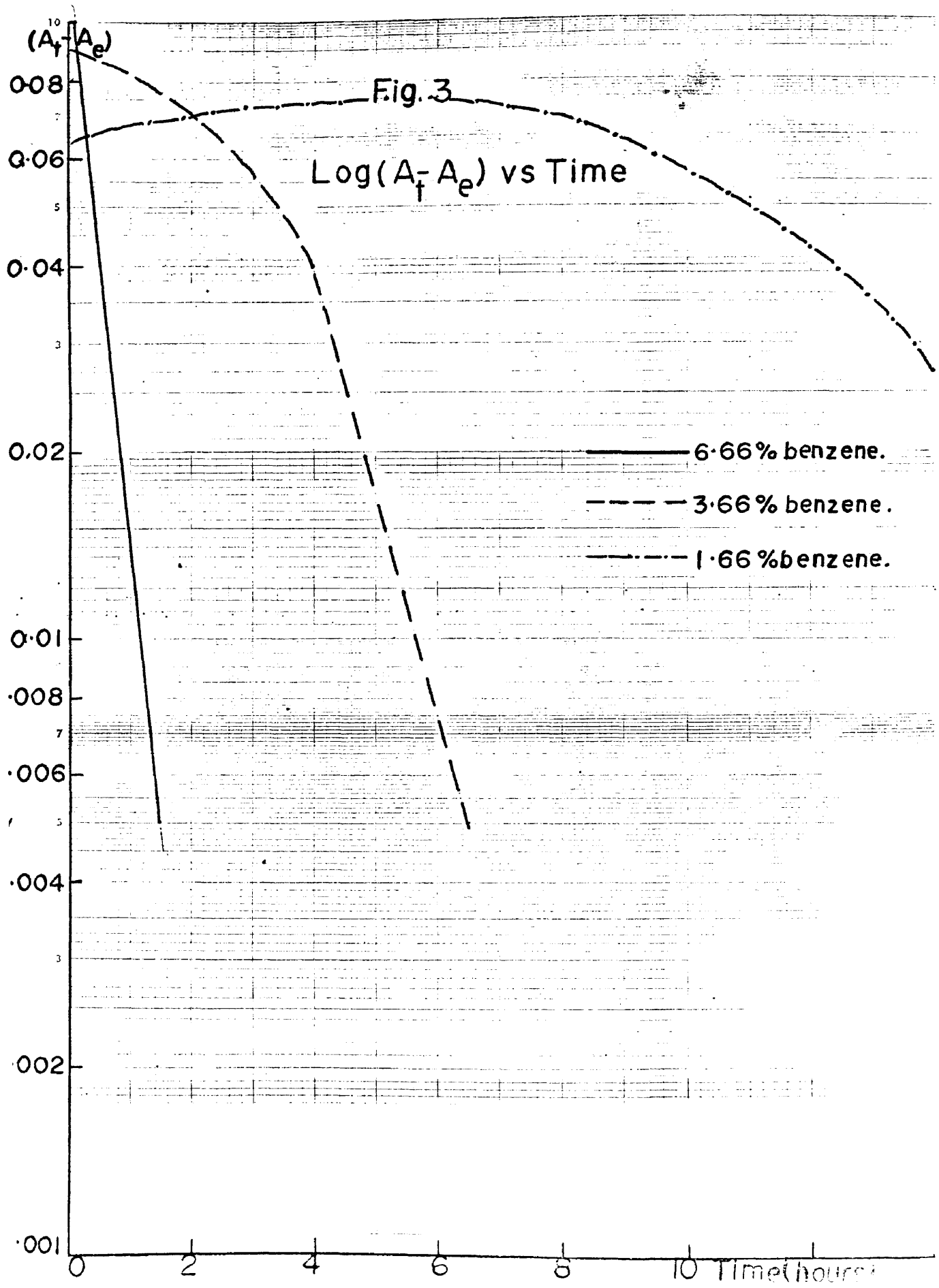


Fig. 3
Log(A_f - A_e) vs Time
(A_f - A_e)
0·08
0·06
0·04
0·02
0·01
·008
·006
·004
·002
·001
6·66% benzene.
3·66% benzene.
1·66% benzene.
0
2
4
6
8
10
Time(hours)

TABLE VII

VOLUMETRIC ANALYSIS FOR Ni
IN THE BENZENE CLATHRATE

TRIAL	PERCENT Ni	
	CLATHRATE I*	II*
1	9.74	9.95
2	9.76	9.95
AVERAGE	9.75	9.95
MOLE RATIO(GUEST/HOST)	0.731	0.582

*Clathrate I and II refers to clathrate formed at minimum and maximum speed of stirring respectively.

TABLE VIII

INTERPLANAR SPACINGS(Å) FOR THE MORE PROMINENT REFLECTIONS FROM THE $Ni(4\text{-mepy})_4(SCN)_2$ COMPLEX AND THE BENZENE CLATHRATE

COMPLEX	CLATHRATE	
	I*	II*
	12.96s	12.70s
8.31s	8.15s	8.04s
7.61w	6.40w	6.80w
	5.89m	5.81m
	5.02m	5.10m
4.98w	4.70w	4.72w
4.30s	4.46s	4.44s
4.07w		
3.86w	3.84m	3.82m
3.55w	3.50m	3.53m

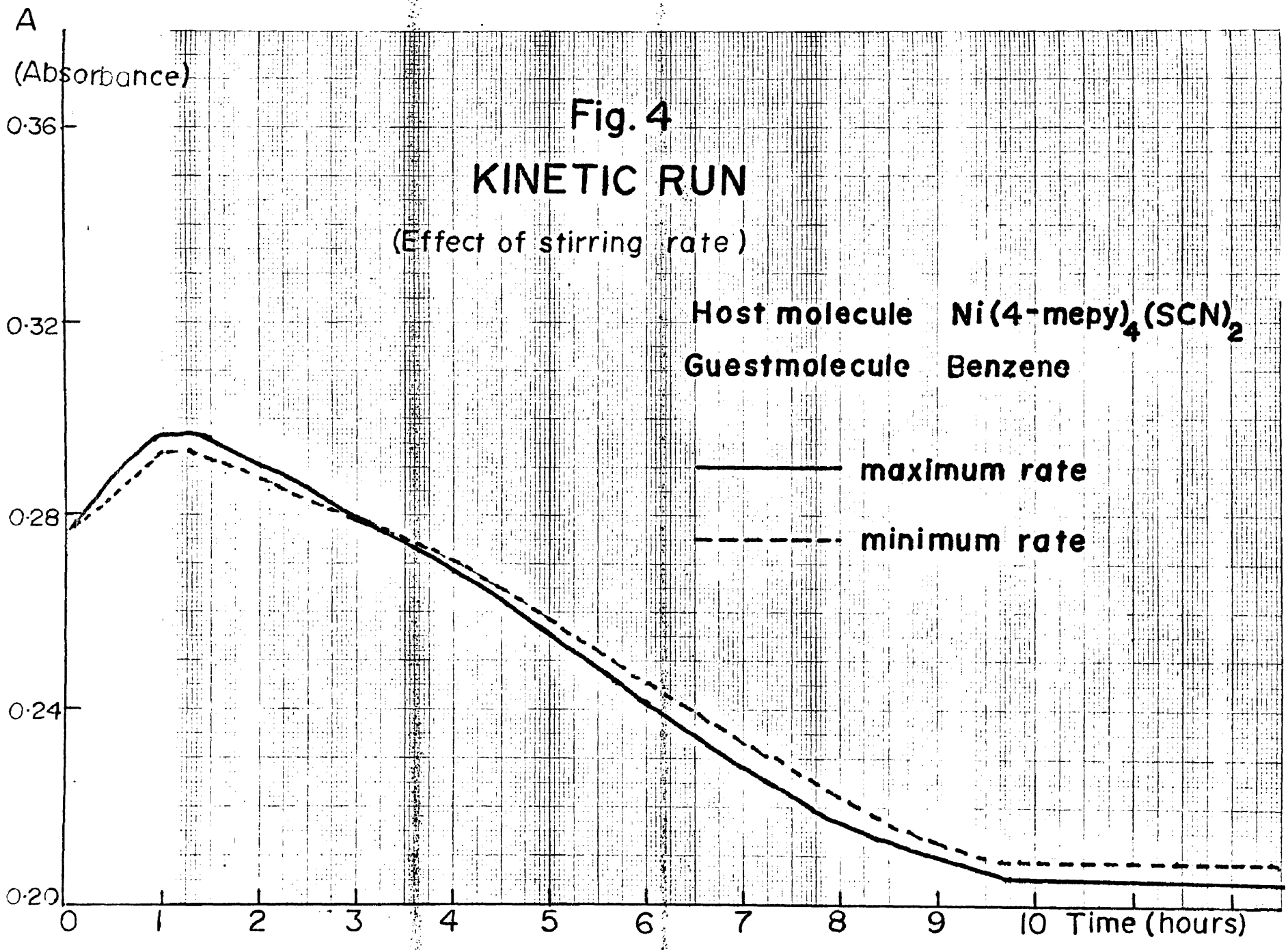
Clathrate I and II refers to clathrate formed at maximum and minimum speeds of stirring.

TABLE IX

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE CLATHRATION REACTION BETWEEN $Ni(4\text{-mepy})_4(SCN)_2$ AND BENZENE AT 25°C

TIME(HOUR)	ABSORBANCE AT 255 mu	
	SAMPLE I	SAMPLE II
0	0.290	0.278
¼	0.296	0.290
½	0.285	0.290
1	0.295	0.276
2	0.281	0.295
3	-	0.284
4	0.272	0.276
6	0.254	0.240
8	0.218	0.214
10	0.208	0.206
12	0.208	0.204
24	0.207	0.204
48	0.207	0.204

Sample I and II refers to clathrate formed at minimum and maximum speed of stirring respectively.


A
(Absorbance)
0·36
0·32
0·28
0·24
0·20
0
1
2
3
4
5
6
7
8
9
10 Time (hours)
Fig. 4
KINETIC RUN
(Effect of stirring rate)
Host molecule Ni(4-mepy)4(SCN)2
Guestmolecule Benzene
maximum rate
minimum rate

Absorbance vs time are shown in Tables VII, VIII, IX, and Figure 4 respectively. From the plotted curves it can be seen that the reaction rate is not effected significantly by stirring speed and hence the possibility of a diffusion controlled rate process was considered unlikely.

Particle size of the host crystals

The effect of the particle size of the suspended host crystals on the clathration process was also studied and it was found that the particle size of the host did not affect the reaction significantly. Tables X, XI, XII, and Figure 5 present the results of the study of the host crystal size.

Concentration of the host

The effect of concentration of the host on the clathration reaction was also studied. The concentration range was varied from 1.83×10^{-2} to 7.31×10^{-2} moles of complex suspended in 300 ml of heptane. The results of the volumetric analyses, the x-ray analyses and kinetic data are presented in Tables XIII, XIV, XV, and a plot of $+\log(A_t - A_\infty)$ vs time is shown in Figure 6. From the shape of the curves obtained it can be concluded that the reaction is not first order in any region of concentration. However, it was observed that 30 gms(5.47×10^{-2} moles) of host in 300 ml heptane took the longest time for completion of the reaction and had the smallest guest to host mole ratio. The concentrations above and below 5.47×10^{-2} moles of host appear to make the reaction go faster and slower respectively.

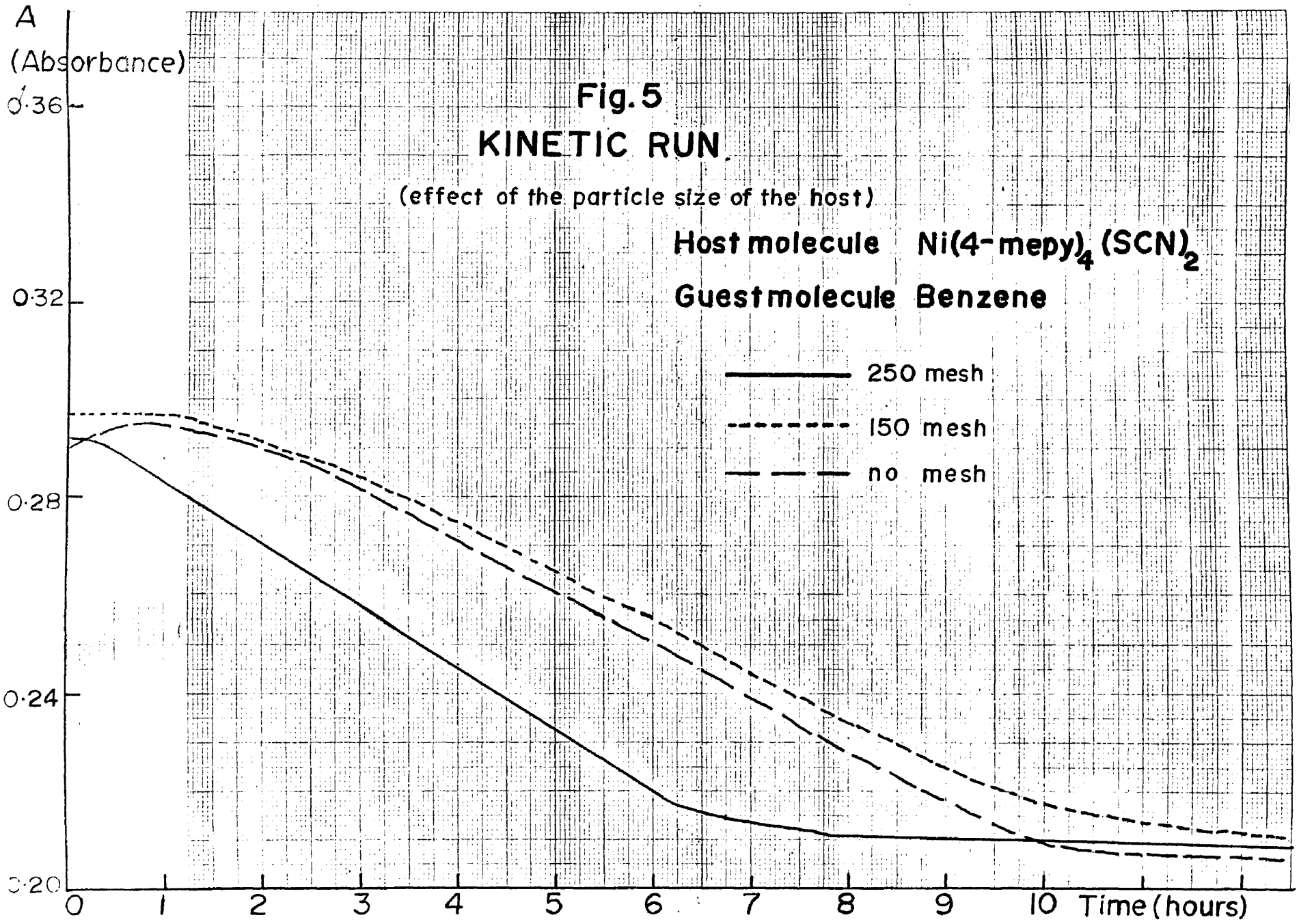

A
(Absorbance)
0·36
0·32
0·28
0·24
0·20
0
1
2
3
4
5
6
7
8
9
10
Time (hours)
Fig. 5
KINETIC RUN
(effect of the particle size of the host)
Host molecule Ni(4-mepy)4 (SCN)2
Guest molecule Benzene
250 mesh
150 mesh
no mesh

TABLE X

VOLUMETRIC ANALYSES FOR Ni
IN THE BENZENE CLATHRATES

TRIAL	PERCENT Ni		
	CLATHRATE I*	II*	III*
1	10.18	9.74	10.10
2	10.18	9.74	10.02
AVERAGE	10.18	9.74	10.06
MOLE RATIO(GUEST/HOST)	0.447	0.738	0.500

*Sample I, II, and III refers to clathrate formed with the complex of variable size and complex which passed through the seive of size 150 and 250 mesh respectively.

TABLE XI

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE CLATHRATION REACTION BETWEEN $Ni(4\text{-mepy})_4(SCN)_2$ AND BENZENE AT 25°C

TIME(HOUR)	ABSORBANCE OF BENZENE AT 255 mu		
	SAMPLE I*	SAMPLE II*	SAMPLE III*
0	0.292	0.297	0.290
¼	0.282	0.288	0.296
½	0.280	0.291	0.295
1	0.283	0.297	0.295
2	0.272	0.288	0.281
3	-	0.272	-
4	0.246	0.255	0.272
6	0.218	0.220	0.254
8	0.211	0.218	0.218
10	0.210	0.215	0.208
12	0.210	0.215	0.208
24	0.209	0.215	0.208
48	0.209	0.215	0.208

*Sample I, II, and III refers to clathrate formed with the complex of size, variable, 150 and 250 mesh respectively.

TABLE XII

INTERPLANAR SPACINGS(Å) FOR THE MORE PROMINENT REFLECTIONS FROM THE $Ni(4\text{-mepy})_4(SCN)_2$ COMPLEX AND THE BENZENE CLATHRATE

COMPLEX	CLATHRATE		
	I*	II*	III*
	13.12s	13.12s	12.70s
8.31s	8.22s	8.44s	8.04s
7.61w	5.95w	6.80w	6.80w
	5.43m	5.80m	5.81m
	4.85m	5.07m	5.10m
4.98w	4.77w	4.73w	4.73w
	4.44s	4.44s	4.44s
4.30s			
4.07w			
3.86w	3.90m	3.86m	3.82m
3.55w	3.59m	3.53m	3.53m

*Clathrate I, II, and III refers to clathrate formed with the complex of variable sixe and complex which passed through the seive of size 150 and 250 mesh respectively

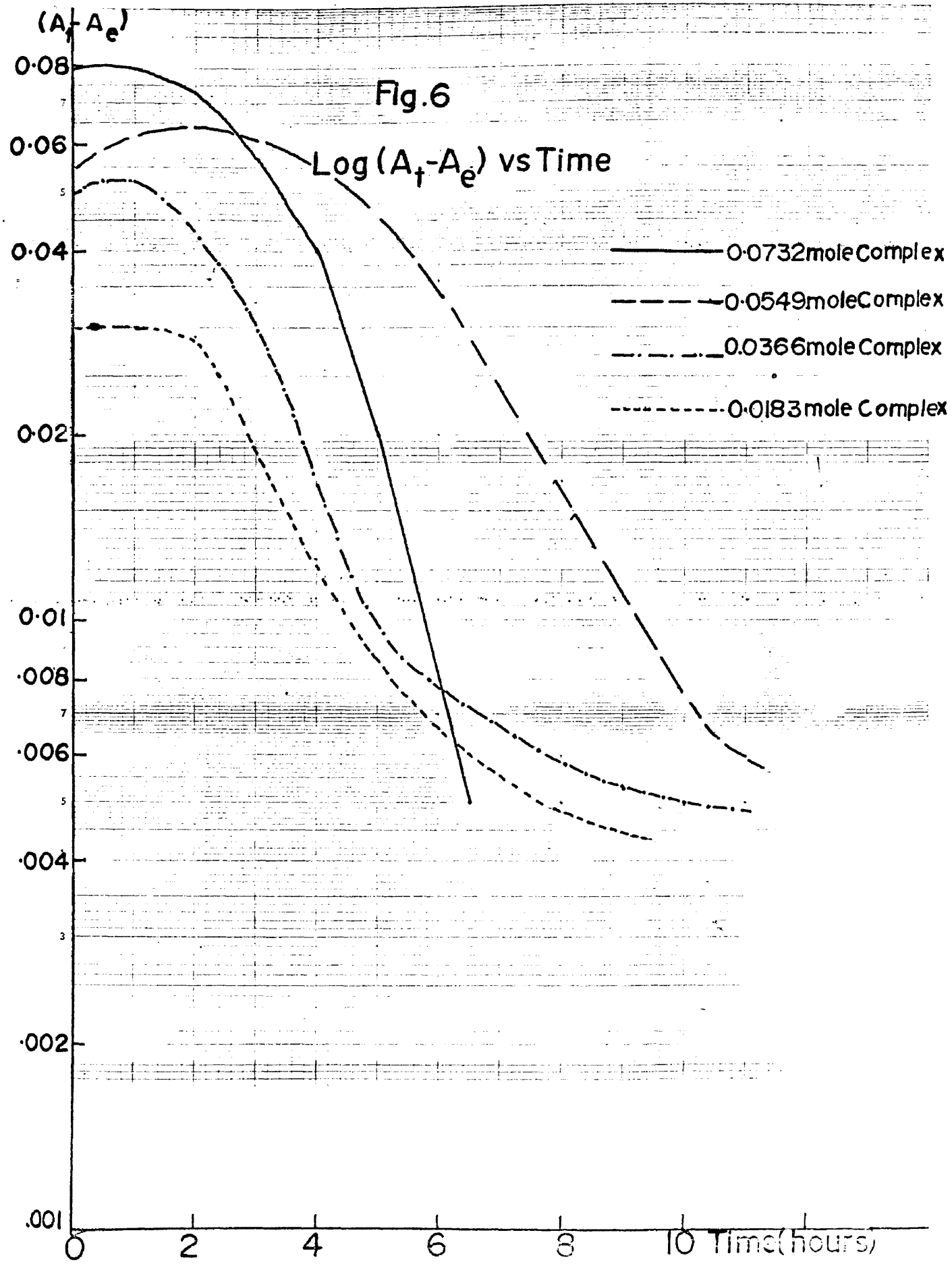

(A_t - A_e)
0·08
0·06
0·04
0·02
0·01
·008
·006
·004
·002
.001
Fig.6
Log (A_t - A_e) vs Time
0·0732mole Complex
0·0549mole Complex
0·0366mole Complex
0·0183mole Complex
0
2
4
6
8
10 Time(hours)

TABLE XIII

VOLUMETRIC ANALYSIS FOR Ni
IN THE BENZENE CLATHRATES

	PERCENT Ni			
TRIAL	CLATHRATE I*	II*	III*	IV*
1	10.55	10.30	10.47	10.17
2	10.49	10.30	10.47	10.02
AVERAGE	10.52	10.30	10.47	10.06
MOLE RATIO(GUEST/HOST)	0.156	0.321	0.192	0.500

*Clathrate I, II, III, and IV refers to the clathrates formed with 10, 20, 30, and 40 grams of complex respectively.

TABLE XIV

CHANGE OF GUEST CONCENTRATION* WITH TIME DURING THE CLATHRATION REACTION BETWEEN $Ni(4\text{-mepy})_4(SCN)_2$ AND BENZENE AT 25°C

TIME(HOUR)	ABSORBANCE OF BENZENE AT 255 mu			
	SAMPLE I	SAMPLE II	SAMPLE III	SAMPLE IV
0	0.285	0.296	0.282	0.297
¼	0.282	0.290	0.289	0.288
½	0.285	0.294	-	0.291
1	0.285	0.298	0.308	0.297
2	0.284	0.284	0.291	0.288
3	0.284	0.280	0.278	0.272
4	0.268	0.256	0.276	0.255
6	0.264	0.254	0.263	0.220
8	0.258	0.252	0.244	0.218
10	0.256	0.251	0.233	0.215
12	0.253	0.246	0.227	0.215
24	0.253	0.246	0.227	0.215
48	0.253	0.246	0.227	0.215

*For calibration curve see Appendix III

TABLE XV

INTERPLANAR SPACINGS(Å) FOR THE MORE PROMINENT REFLECTIONS FROM THE $Ni(4\text{-mepy})_4(SCN)_2$ COMPLEX AND THE BENZENE CLATHRATE

COMPLEX	CLATHRATE			
	I*	II*	III*	IV*
	12.63s	13.06s	13.18s	13.11s
8.31s	8.04s	8.04s	8.06s	8.04s
7.61w	6.94w	6.81w	6.83w	6.80w
	5.81m	5.82m	5.82m	5.80m
	5.06m	5.07m	5.08m	5.06m
4.98w	4.72w	4.73w	4.75w	4.73w
	4.49s	4.44s	4.50s	4.44s
4.30s				
4.07w				
3.86w	3.82m	3.81m	3.84m	3.86m
3.55w	3.53m	3.53m	3.54m	3.52m

* Clathrate I, II, III, and IV refers to the clathrate formed with 10, 20, 30, and 40 grams of complex respectively.

Test of reversibility

Minton in her thesis(20) presents evidence to indicate that the clathration reaction is a reversible reaction. Since it was found in this laboratory that the clathration reaction is not first order, it was decided to verify that the reaction is indeed reversible. Two methods were devised for this test. The first method consisted of adding clathrate to pure heptane and following any change in the guest concentration. The second method consisted of adding clathrate to heptane already containing some benzene(the concentration of benzene used was the same as the equilibrium concentration found during the clathration process). The results are presented in Tables XVI through XVIII and Figure 7. From the plotted data it appears that the clathration process is not a reversible one in the case of benzene as the guest molecule.

From the results presented on the previous pages, the following mechanisim for the clathration process is proposed:

$$\text{Complex}(\alpha) \rightleftharpoons \text{Complex}(\beta) \qquad (1)$$

$$\text{Complex}(\beta) + \text{Guest} \longrightarrow \text{Clathrate} \qquad (2)$$

Equation (1) represents simply a lattice change in the crystal structure of the complex brought about by the guest, and is not affected by variations such as solvent, temperature, particle size of the complex crystals, stirring rate etc, (however it is greatly affected by the concentration of the guest). The lattice change from α to β has been proved conclusively by x-ray analysis as presented in various tables

TABLE XVI

VOLUMETRIC ANALYSES FOR Ni
IN THE SOLID LEFT OVER AFTER
REVERSE OF CLATHRATION STUDY

	PERCENT Ni	
TRIAL	SAMPLE I*	SAMPLE II*
1	10.41	10.11
2	10.41	10.11
AVERAGE	10.41	10.11
MOLE RATIO(GUEST/HOST)**	.234	0.462

*Sample I and II refers to the reverse of the clathration reaction studied with and without benzene in the reaction solution respectively.

**(GUEST/HOST) mole ratio of clathrate used in this reaction were 0.283 and 0.470 respectively.

TABLE XVII

CHANGE OF GUEST CONCENTRATION WITH TIME DURING THE REVERSE OF CLATHRATION REACTION OF $Ni(4\text{-mepy})_4(SCN)_2 \cdot$BENZENE AT 25°C

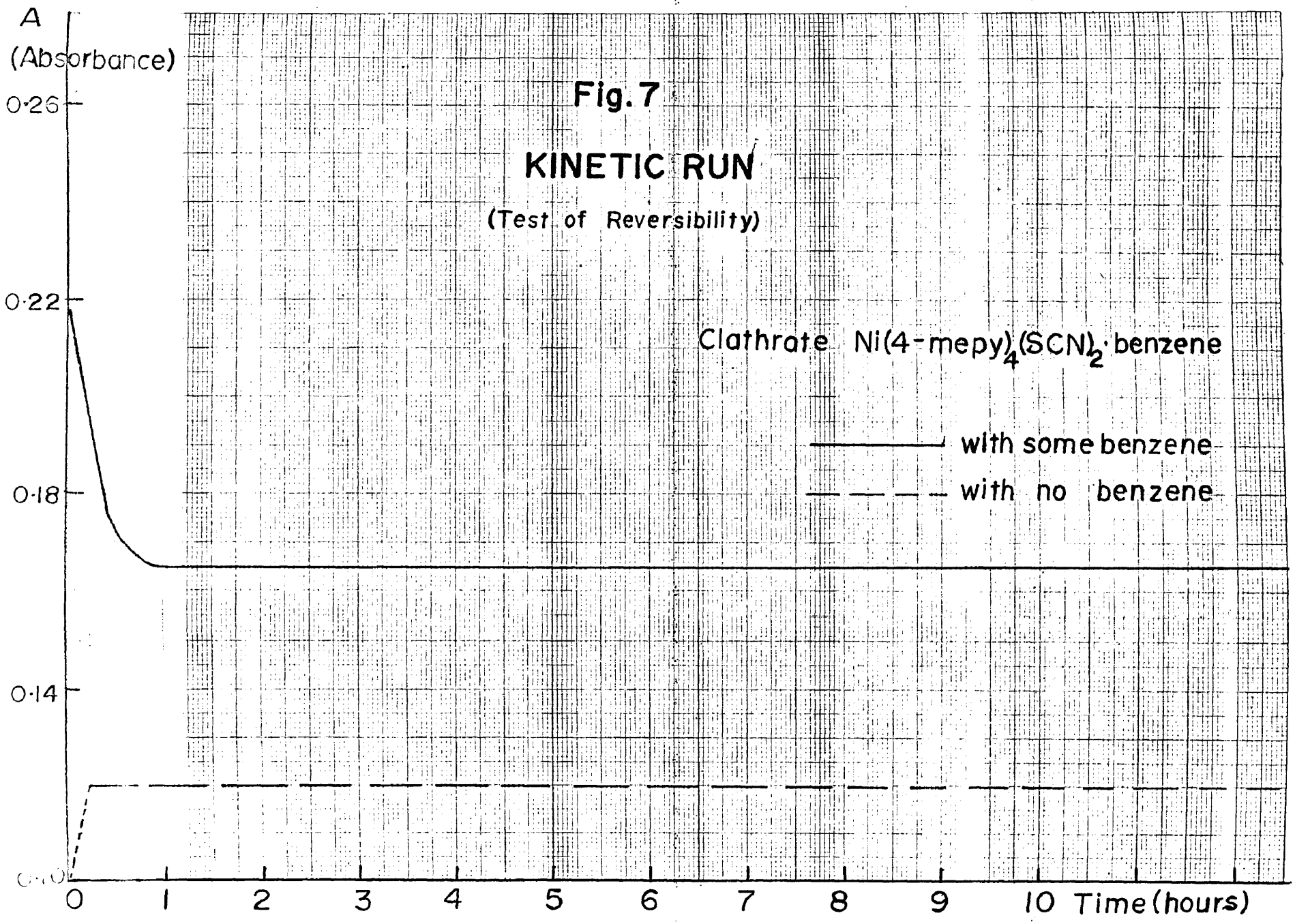
TIME(HOUR)	ABSORBANCE AT 255 mu	
	SAMPLE I*	SAMPLE II*
0	0.168	0.0292
¼	0.160	0.0287
½	0.170	0.0291
1	0.164	0.0292
2	0.167	0.0294
3	0.170	0.0293
4	0.170	0.0292
6	0.167	0.0292
8	0.167	0.0292
10	0.165	0.0291
12	0.170	0.0293
24	0.167	0.0292
48	0.167	0.0292
60	0.167	0.0292

*Sample I and II refers to the reverse of the clathration reaction studied with and without benzene in the reaction solution respectively.

TABLE XVIII

INTERPLANAR SPACINGS(Å) FOR THE MORE PROMINENT REFLECTIONS FROM THE SOLID LEFT OVER AFTER REVERSE OF CLATHRATION STUDY

COMPLEX	CLATHRATE	
	I*	II*
	12.69	12.67
8.31	8.02	8.06
7.61	6.79	6.77
	5.80	6.23
	5.05	5.02
4.98	4.77	4.74
4.30	4.44	4.51
4.07		
3.86	3.86	3.87
3.55	3.45	3.57


A
(Absorbance)
0·26
0·22
0·18
0·14
0·10
0
1
2
3
4
5
6
7
8
9
10 Time (hours)
Fig. 7
KINETIC RUN
(Test of Reversibility)
Clathrate Ni(4-mepy)4(SCN)2·benzene
with some benzene
with no benzene

in this thesis and elsewhere. This result is in exact agreement with the work of Hart and Smith(16). Equation(2) appears to be second order. If the reaction were to be first order it has to depend on the concentration of either the complex or the guest. As seen in the previous sections the reaction depends mainly on the concentration of the guest and to some extent on the concentration of complex in the reaction mixture. At higher concentrations of the guest the reaction is first order and very fast. At low concentration of the guest the reaction may be second order. Thus, the reaction may be in fact between first and second order for most of the kinetic runs. The fact that the clathration process is not first-order or reversible was again confirmed by other workers in this laboratory(42).

Calorimetric Studies and Magnetic Susceptibility Results

The first calorimetric studies on Werner complex clathrates were reported by Hart and Smith(16). As a part of their studies it was shown that there is a linear relationship between the heat of formation and the guest to host mole ratio. Minton(20) extended their studies using toluene and ethylbenzene in a study of prefrential clathration. Minton also reported ΔS values for the clathration process from calorimetric studies. Casellato and Casu(3) found an apparent relationship between ∂C-H shifts and Hammett Substituent Constants of clathrated guest molecules. According to Tamres(36) there should be a linear relationship between the heat of clathration and the

Hammett Substituent Constant if there is a charge transfer type of interaction between guest and host in the clathrate. In order to verify this relationship a detailed investigation of the heat of formation of various clathrates was carried out. The heat of solution of a number of clathrates and the heat of mixing of a number of guests in a 1% solution of 4-methyl pyridine in dichloromethane was determined. The heats of formation were computed using the method of Logan and others(41). Dichloromethane is used as the solvent because $Ni(4\text{-mepy})_4(SCN)_2$ retains its octahedral configuration in the presence of an excess of 4-methylpyridine in dichloromethane(37). The results of the heat of mixing of guests, heat of solution and the heat of formation of clathrates formed by the complex $Ni(4\text{-mepy})_4(SCN)_2$ are presented in Tables XIX, XX, XXI respectively. A plot of ΔH_f vs the sum of Hammett constants, sigma-meta and sigma-para($\sigma_m + \sigma_p$), for the substituents on the guest molecules was drawn. From Figure 8 it is clear that only a very few fall on a straight line indicating that interaction between guest and host is probably not of the charge-transfer type. It is also interesting to note that halo-hydrocarbon guests and guests having a substituent with a lone pair of electrons deviated far from the line indicating there is apparently some other interaction in addition to a possible charge-transfer type. A plot of ΔH_f vs $\Sigma\Delta\nu$ was also drawn. A large deviation from linearity again supports the above conclusion. Table XXII includes a

TABLE XIX

HEAT OF MIXING OF VARIOUS GUESTS IN A 1% SOLUTION OF 4-METHYLPYRIDINE IN DICHLOROMETHANE AT 25°C

GUEST	$-\Delta H_{298}$ Kcal/mole
p-dichlorobenzene	2.583
aniline	0.556
iodobenzene	0.213
bromobenzene	0.082
chlorobenzene	0.056
benzene	-0.094
styrene	-0.105
ethylbenzene	-0.119
p-xylene	-0.204
toluene	-0.240
nitrobenzene	-0.299
methoxybenzene	-0.437
phenol	-0.552

TABLE XX

HEAT OF SOLUTION OF CLATHRATES IN A 1% SOLUTION OF 4-METHYLPYRIDINE IN DICHLOROMETHANE AT 25°C

$$\text{CLATHRATE}(\beta) + \text{SOLVENT} \longrightarrow \text{COMPLEX}(\alpha) + \text{GUEST}(l)$$

GUEST	$-\Delta H_{298}$ Kcal/mole
p-dichlorobenzene	2.58
aniline	6.38
iodobenzene	6.74
bromobenzene	4.43
chlorobenzene	3.91
benzene	3.18
styrene	5.78
ethylbenzene	2.55
p-xylene	6.09
toluene	1.97
nitrobenzene	2.57
methoxybenzene	2.18
phenol	3.75

TABLE XXI

HEAT OF FORMATION OF CLATHRATES
1% SOLUTION OF 4-METHYL PYRIDINE
IN DICHLOROMETHANE AT 25°C

$$\text{COMPLEX}(\alpha) + \text{GUEST}(1) \longrightarrow \text{CLATHRATE}(\beta)$$

GUEST	ΔH_{298} Kcals/mole
p-dicholorobenzene	3.59
aniline	8.46
iodobenzene	10.06
bromobenzene	7.89
chlorobenzene	7.38
benzene	6.81
styrene	9.42
ethyl benzene	6.21
p-xylene	9.65
toluene	5.75
nitrobenzene	6.41
methoxybenzene	6.16
phenol	7.84

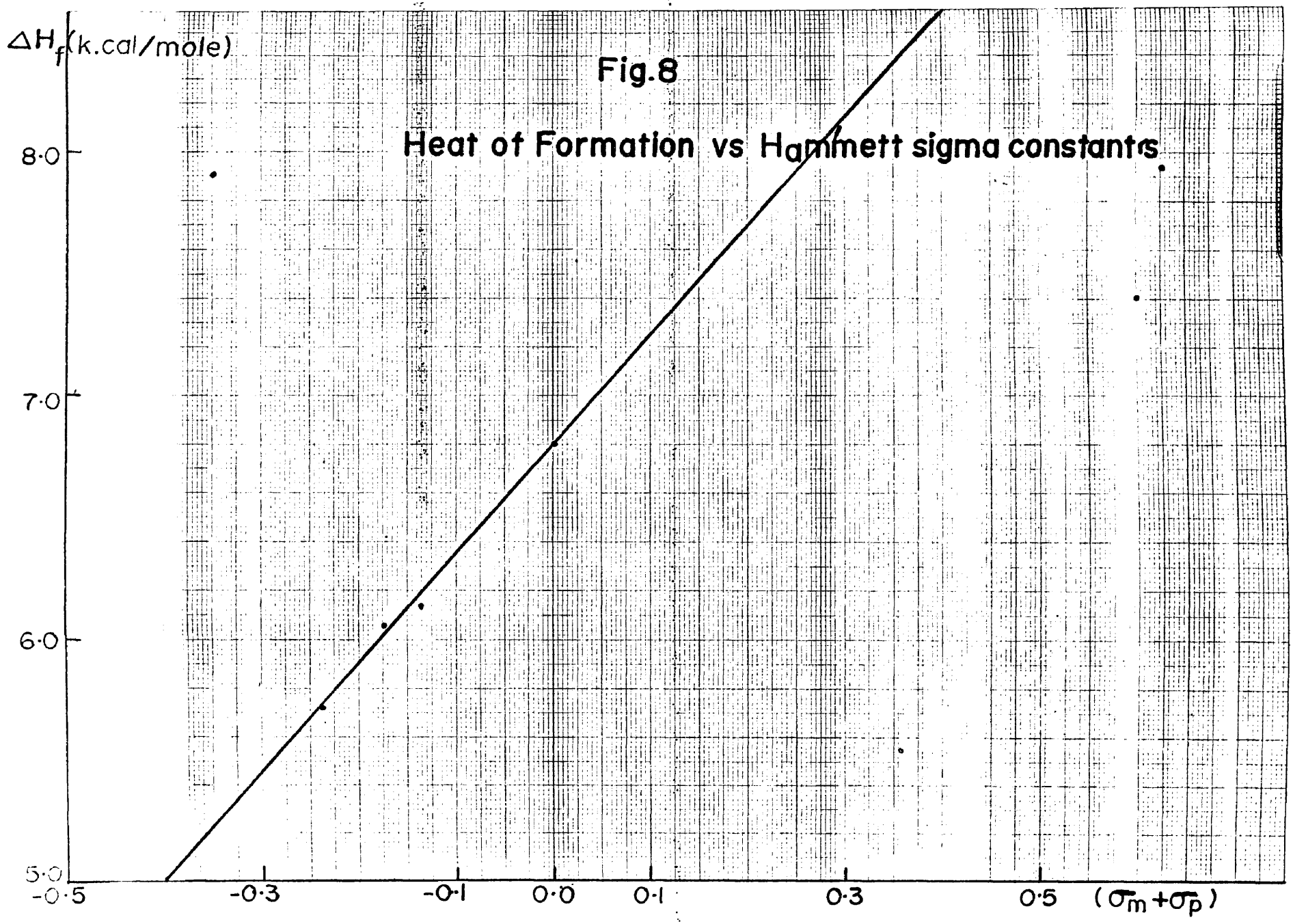


Fig.8
Heat of Formation vs Hammett sigma constants
ΔHf (k.cal/mole)
8·0
7·0
6·0
5·0
-0·5
-0·3
-0·1
0·0
0·1
0·3
0·5
(σm+σp)

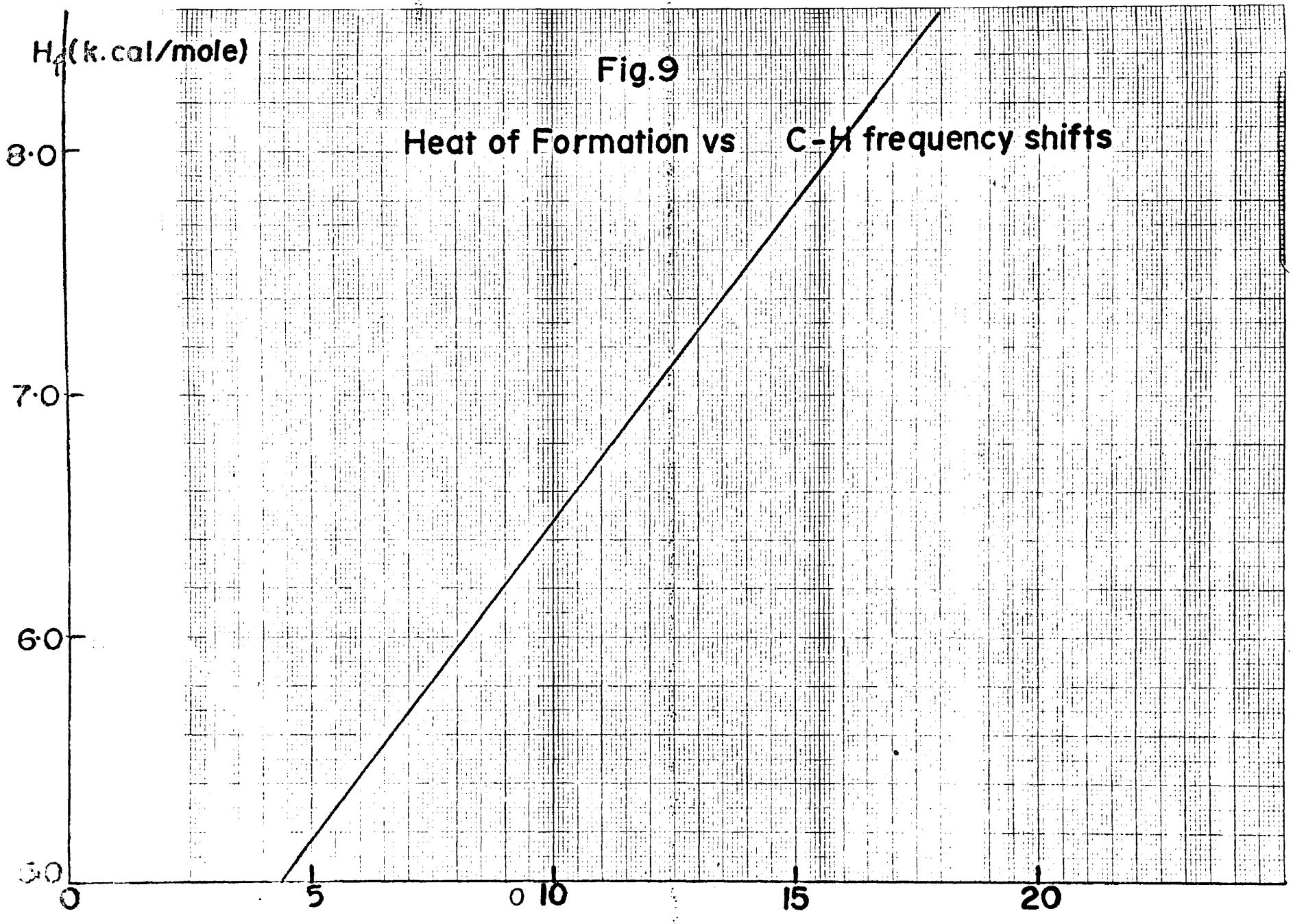


Fig.9
Heat of Formation vs C-H frequency shifts
H_f (k.cal/mole)
8·0
7·0
6·0
5·0
0
5
10
15
20

list of heats of formation, guest to host mole ratios, $\Sigma\Delta\mathcal{J}$ values and $(\sigma_m + \sigma_p)$ values of the guests used. ΔS values for the process could not be evaluated since the clathration is apparently not a reversible process. The lack of experimental knowledge at present also prohibited the evaluation of ΔG for the process. The type of interaction between guest and host thus remains unknown following the heat of clathration study.

The magnetic susceptibility determination for the complex $Ni(4\text{-mepy})_4(SCN)_2$ and its benzene clathrate gave values of 3.88×10^{-3}/mole and 3.81×10^{-3}/mole respectively at room temperature($\approx$25°C). The calculation of the number of unpaired electrons associated with the nickel atom using the above values of magnetic susceptibilities showed two unpaired electrons in both cases. This would indicate that the unpaired electrons about the nickel atom do not participate significantly in any interaction with the guest molecule in the clathrate.

TABLE XXII

GUEST CONTENT, HEATS OF FORMATION AND δC-H FREQUENCY SHIFTS OF SUBSTITUTED BENZENES CLATHRATED IN THE β-LATTICE OF $Ni(4\text{-mepy})_4(SCN)_2$

R-⟨⟩-R'		HAMMETT** SUBSTITUENT CONSTANTS ($\sigma_m+\sigma_p$)	GUEST TO HOST MOLE RATIO	HEATS OF FORMATION AT 25°C	$\Sigma\Delta\nu$*
NH_2	H	-0.82	1.49	-8.46	18.4
OH	H	-0.35	1.17	-7.84	14.5
CH_3	H	-0.24	0.65	-5.75	7.9
C_2H_5	H	-0.22	1.04	-6.21	4.6
OCH_3	H	-0.15	0.94	-6.09	9.8
H	H	0.00	0.87	-6.81	-
Cl	H	0.60	0.80	-7.38	13.5
Br	H	0.62	0.92	-7.89	12.8
I	H	0.64	0.16	-10.06	24.7
NO_2	H	1.49	0.64	-6.41	17.5
$-CH=CH_2$	H	-	1.38	-9.42	14.0
Cl	Cl	0.60	0.99	-3.59	13.6
CH_3	CH_3	0.24	1.00	-9.65	8

*F. Casellato and B. Casu, Spectro Chimica, 25A, 1407(1969).

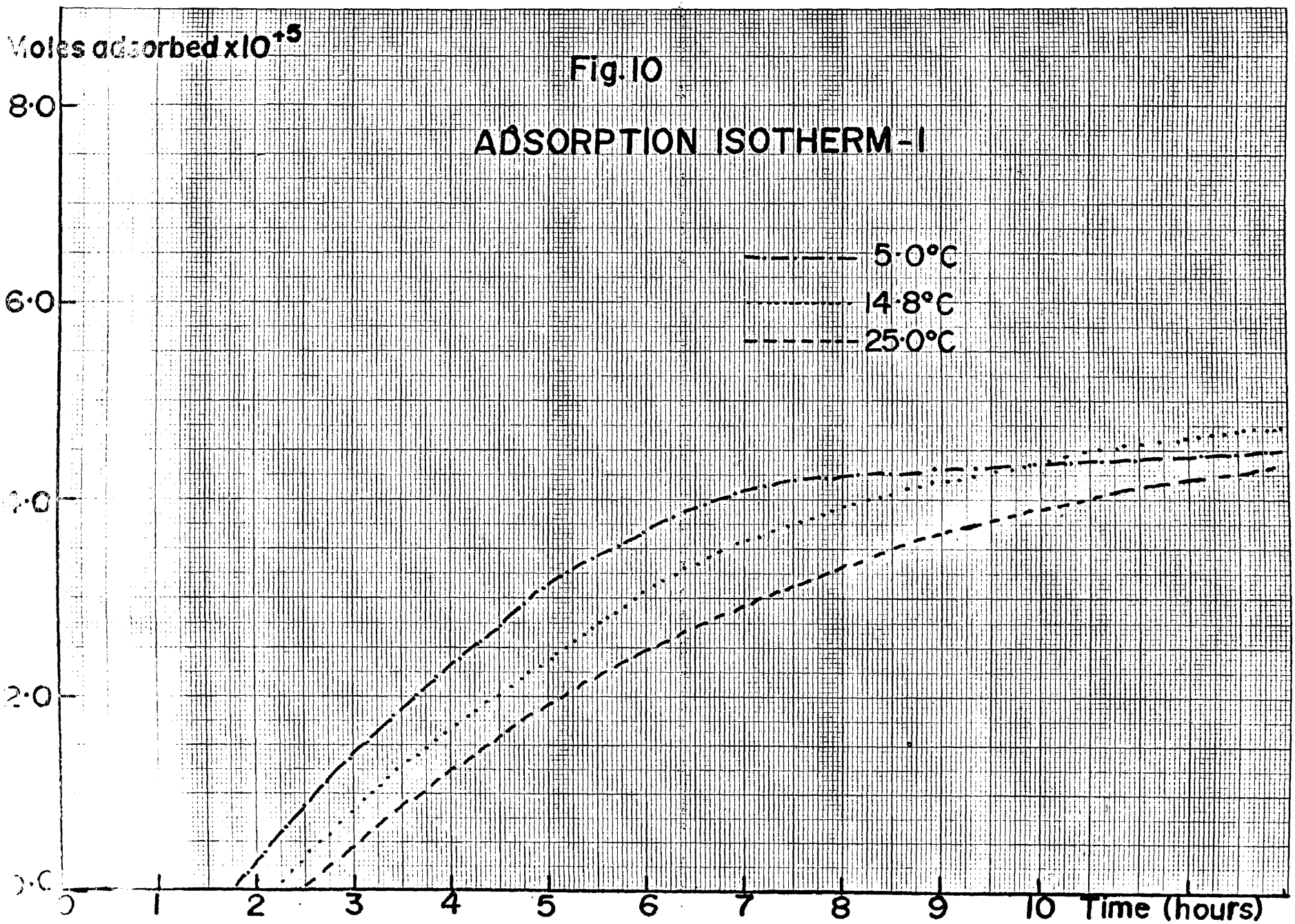
**D. H. McDaniel and H. C. Brown, J. Org. Chem., 23, 420(1958).

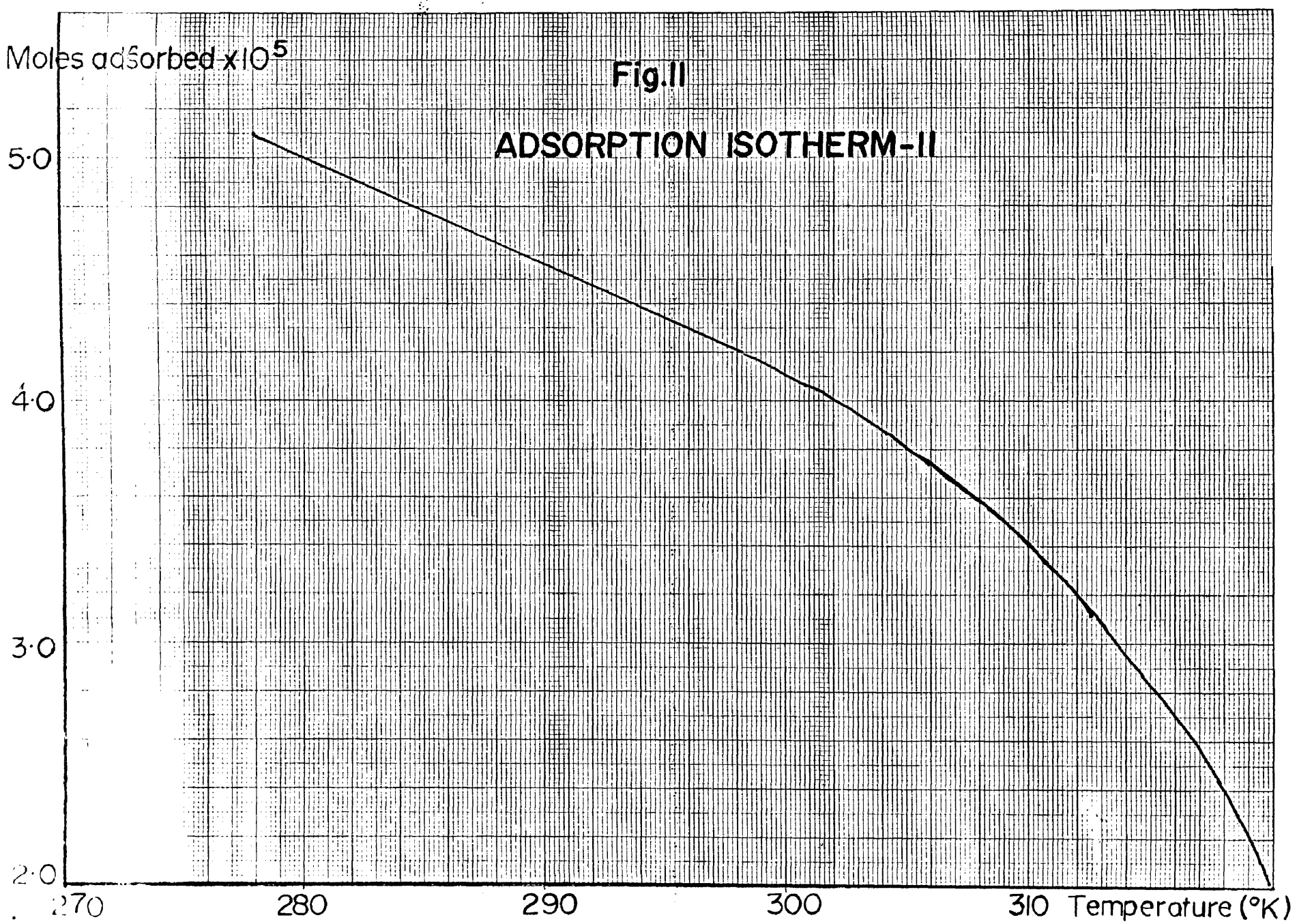
GENERAL SUMMARY

GENERAL SUMMARY

Clathrates of Werner Complexes have been studied mainly because of their ability to separate various organic isomers. Previous work in this laboratory has included the preparation and kinetic studies of a number of clathrates utilizing complexes formed by first row transistion metals. The study presented here consists of further investigations of the kinetics of the clathration reaction, heats of formation and magnetic susceptibility measurements.

Due to the conflicting results obtained in this laboratory(18) and in others(20), an extensive study of the kinetics of the clathration process was undertaken. Detailed studies of factors such as temperature, stirring rate, concentration of the guest concentration of the host, and particle size of the complex crystals were completed. The results from these studies revealed that the clathration reaction between $Ni(4\text{-mepy})_4(SCN)_2$ and benzene is other than a first order, reversible reaction as was previously reported. Therefore, a modified mechanism was proposed. However, the new mechanism was also unable to account for all the results obtained. It was also postulated that the "reaction" between $Ni(4\text{-mepy})_4(SCN)_2$ and benzene might be a simple adsorption process. There is already some indication in the literature that what has been assumed to be clathration may in somes cases be an adsorption process(45). To test this hypothesis adsorption isotherms were drawn and are shown in Figures 10, 11, 12, and 13. From these figures and Tables VII and X it appears that an adsorption process could


Moles adsorbed x10⁻⁵
Fig. 10
ADSORPTION ISOTHERM-I
5·0°C
14·8°C
25·0°C
8·0
6·0
2·0
0·0
0
1
2
3
4
5
6
7
8
9
10
Time (hours)


Moles adsorbed x10^5
Fig.II
ADSORPTION ISOTHERM-II
5·0
4·0
3·0
2·0
270
280
290
300
310 Temperature (°K)

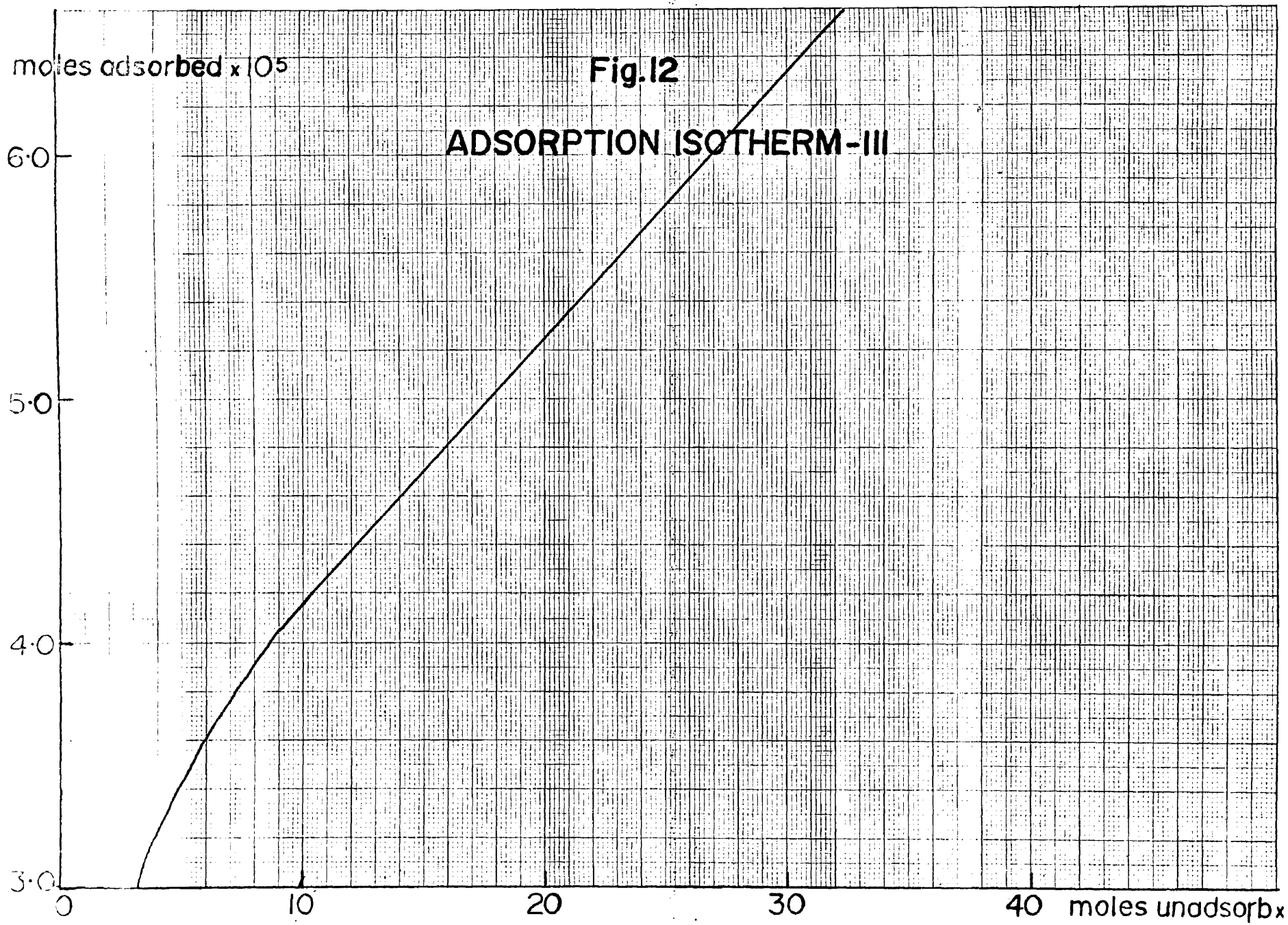
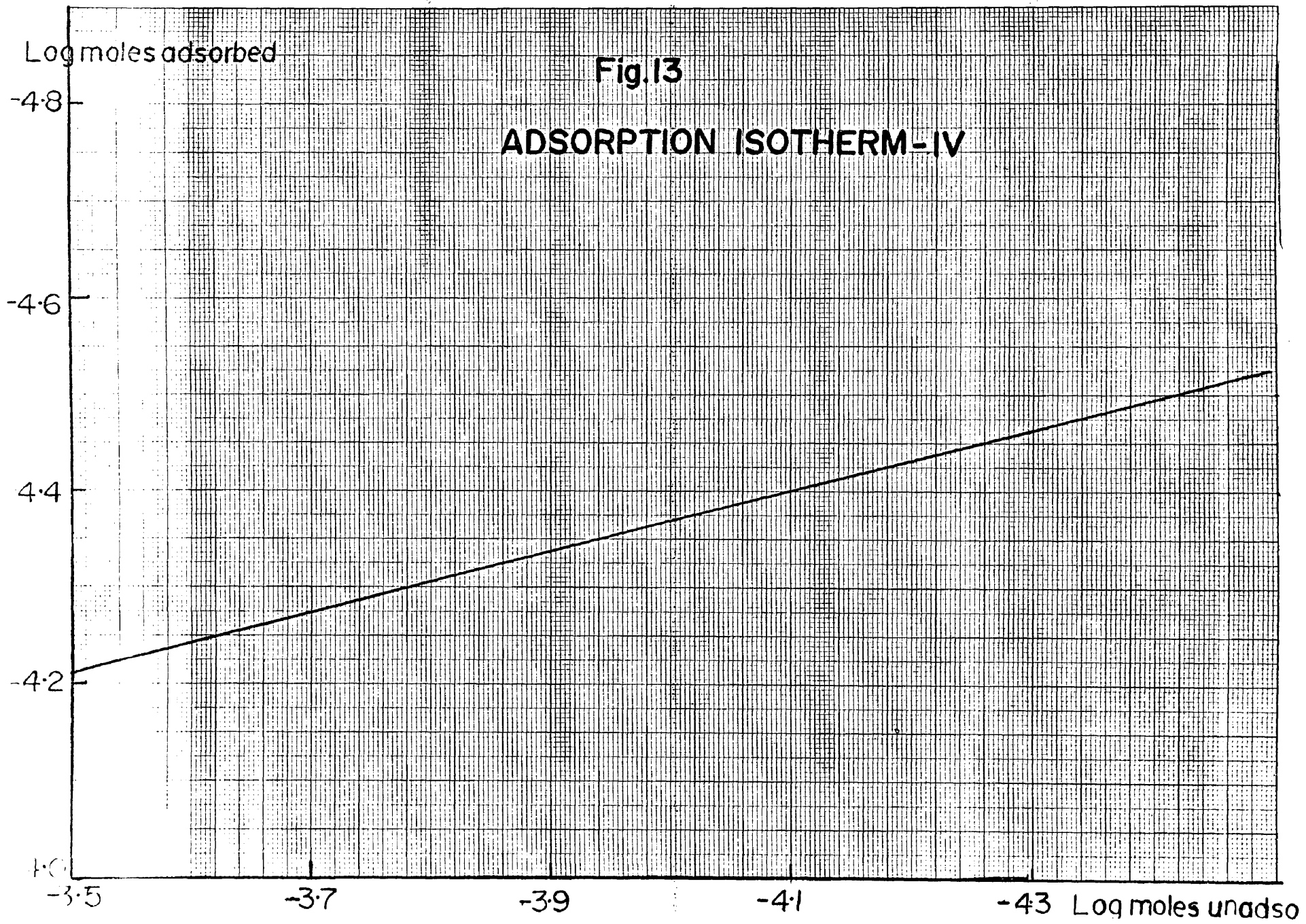


Fig.12
ADSORPTION ISOTHERM-III
moles adsorbed x 10⁵
6·0
5·0
4·0
3·0
0
10
20
30
40
moles unadsorb x 10


Log moles adsorbed
Fig.13
ADSORPTION ISOTHERM-IV
-4·8
-4·6
4·4
-4·2
-3·5
-3·7
-3·9
-4·1
-43
Log moles unadso

explain the data reported in this thesis. However, more detailed studies are needed to conclusively prove it to be an adsorption process.

The results of the x-ray powder diffraction measurements confirm the lattice change($\alpha \rightarrow \beta$) in going from complex to clathrate.

The heat of solution measurements reveal that the heat of formation of various clathrates is about 6-8 k.cals/mole, indicating that the interaction between the guest and the host in the clathrate may be either charge-transfer type or simple Vander-Waals forces. This value for the heat of formation would also be in the range for simple physical adsorption forces. Magnetic susceptibility measurements confirm that the environment about the nickel atom does not change as a result of clathration.

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APPENDICES

Appendix I

Calculation of Guest to Host Mole Ratio in Clathrates

% of Ni in $Ni(4\text{-mepy})_4(SCN)_2$ = (58.71/547.34)X100 = 10.73

% of Ni in benzene clathrate

$Ni(4\text{-mepy})_4(SCN)_2 \cdot \phi H$ = (58.71/625.45)X(100) = 9.39

(assuming 1:1 mole ratio)

% of benzene in the clathrate

$Ni(4\text{-mepy})_4(SCN)_2 \cdot \phi H$ = (78.11/625.45)X(100) = 12.49

(assuming 1:1 mole ratio)

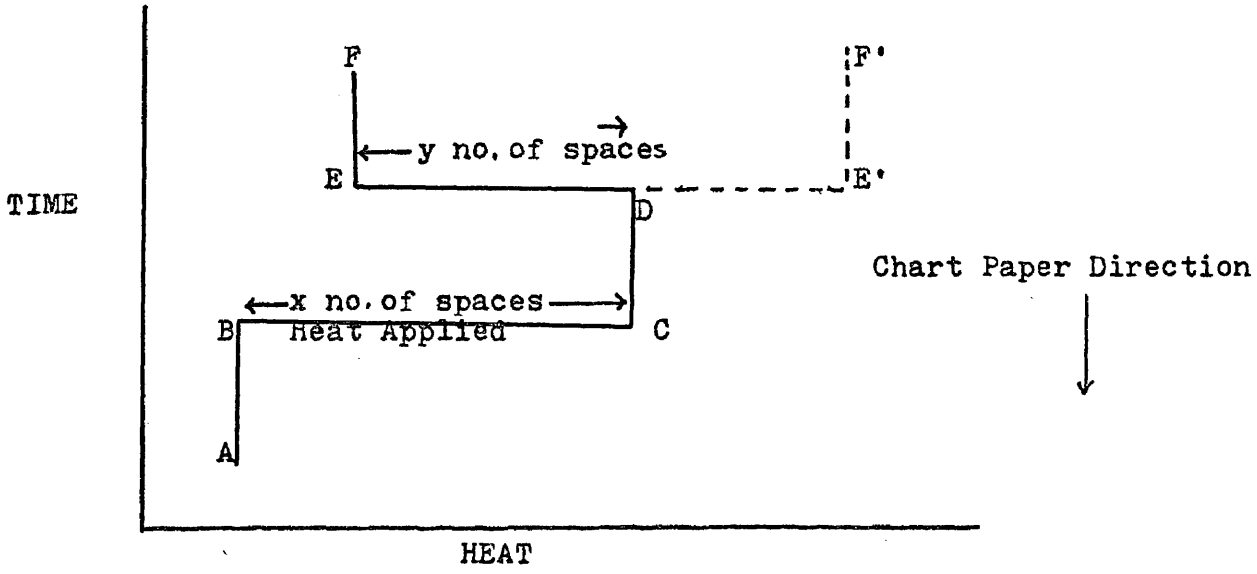
If, for example, 10.20% Ni is found in the clathrate, then 'X' the guest to host mole ratio is given by:

$$\frac{10.73 - 9.39}{1} = \frac{10.73 - 10.20}{X}$$

$$X = \frac{0.53}{1.34} = 0.40$$

Appendix II

Calculation of Heat of Solution from experimental data.



The electrical heat introduced(applied) to the solution in calories is:

$$Q_H = \frac{I^2RT}{4.184}$$

Where $I = \frac{E}{R}$

E = potential applied across the terminals of the heater.

R = resistance of the potentiometer

R = resistance of the heater

t = time of heating in seconds

4.184 = conversion of joules to gram-calorie

x number of spaces = Q_H cals

$\therefore$ 1 space = $\frac{Q_H}{x}$ cals/space

$\pm \Delta H = (Q_H/x)y = \cdots\cdots\cdots$ cals/gm where

ΔH = change in heat due to the addition of the sample.

Calculation of the Heat of Formation

The equation for clathration reaction is:

$$\text{Complex(s)} + \text{Guest(l)} \longrightarrow \text{Clathrate(s)} + Q$$

heat of formation(ΔH_F) is given by

$$\Delta H_F = L_{w.c.} + L_G - L_c$$

ΔH_F = heat of formation of clathrate in 1% solution of 4-methylpyridine in dichloromethane at 25°C.

$L_{w.c.}$ = heat of solution of Werner Complex

L_G = heat of mixing of Guest

L_c = heat of solution of clathrate

Appendix III

Calibration Curve

The absorbance of benzene in n-heptane was obtained on the Beckman DB-G Spectrophotometer using matched silica cells. Spectroquality benzene was used while the purity of the solvent, n-heptane, was obtained spectrophotometrically and gave a straight baseline from 320 mμ to 245 mμ.

Data Plotted:

Number of λ's* of benzene per 100 ml of heptane	Concentration+	A(Absorbance)
0.5	5.597	0.01
2.5	27.98	0.055
5.0	55.97	0.115
10.0	111.90	2.00
15.0	167.90	0.34

*(1λ = 0.001ml)

+ moles of benzene per liter of heptane $X10^5$

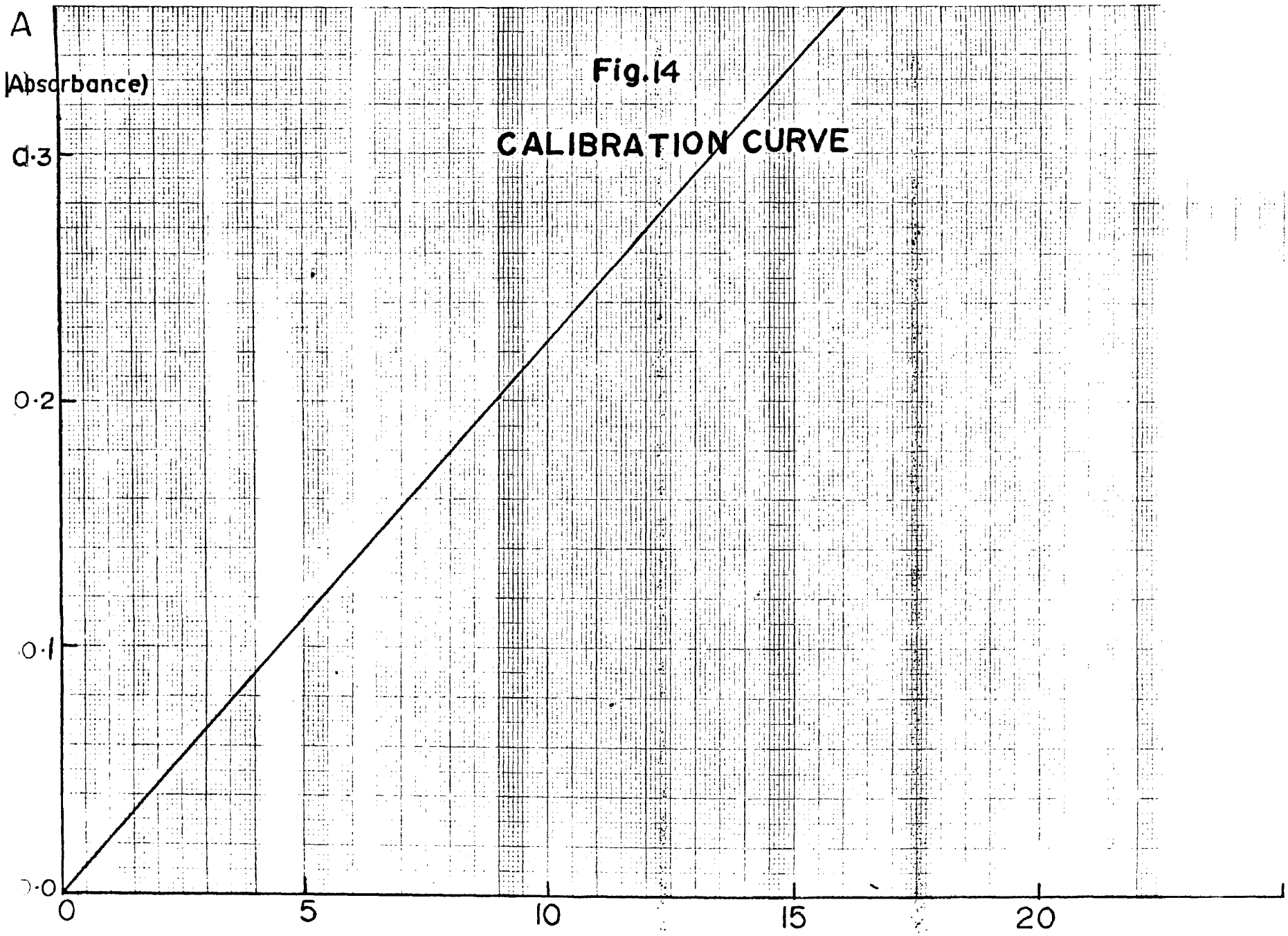


Fig.14

CALIBRATION CURVE

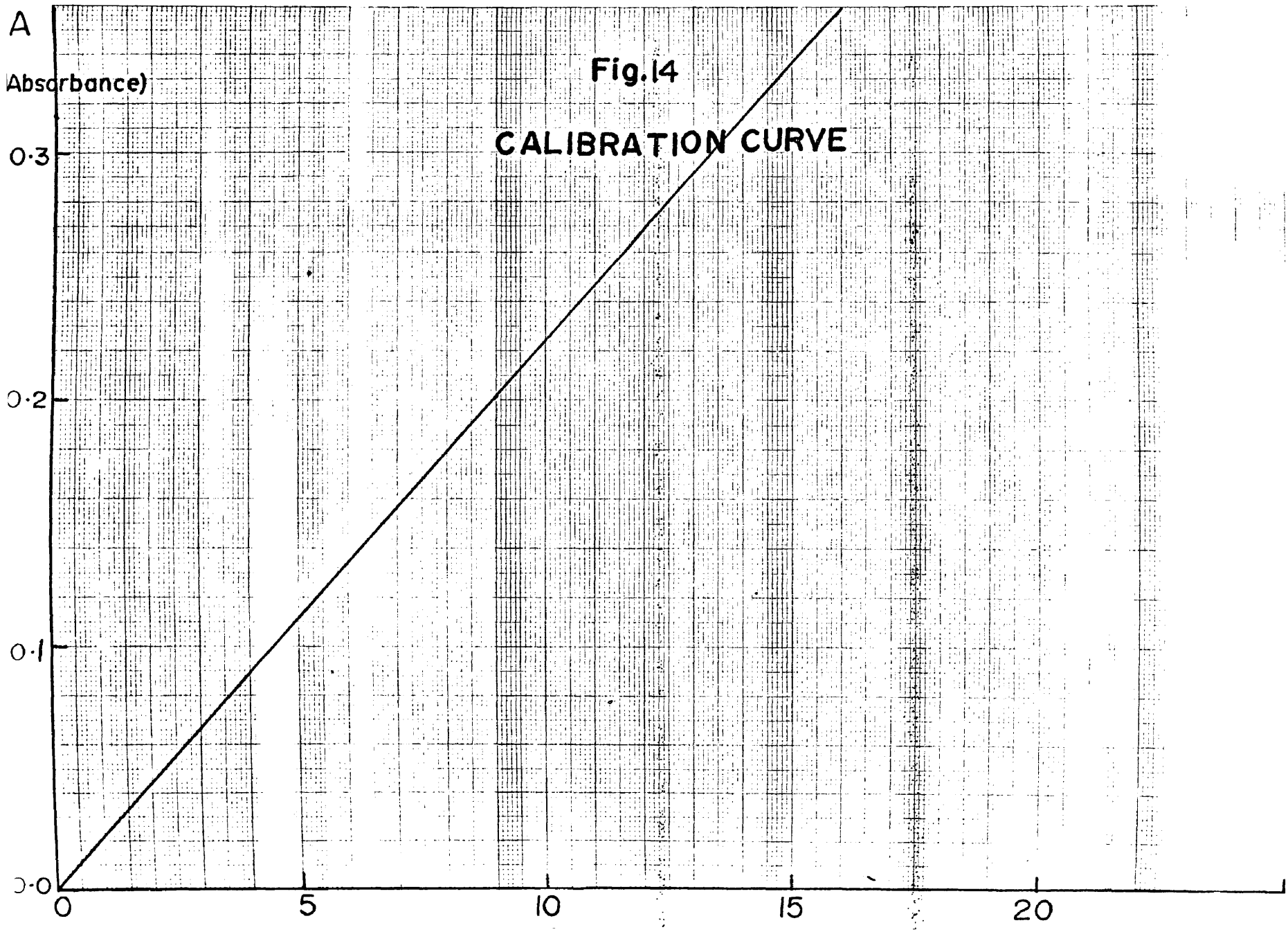


Fig.14

CALIBRATION CURVE